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EXPLOITATION OF THE SOL-GEL ROUTE IN PROCESSING OF CERAMICS AND COMPOSITES

FINAL REPORT

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base, DC 20332

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Submitted by

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I. Program Goals

The goal of this program was to explore and develop novel processing techniques for ceramics via the sol-gel route.

II. Progress to Date

A. Introduction

The sol-gel process for making ceramic powders from solutions-gels, and especially the use of alkoxide precursors, and their subsequent conversion of gels to ultrahomogeneous glass was developed at Penn State by the P.I. and his students (1-5). While the above pioneering work blanketed the science of compositional aspects (phase equilibria) of ceramic and glasses made by sol-gel it did not address the technological applications which started 15 years later with the innovative Oak Ridge process for shaping $\text{UO}_2\text{-ThO}_2$ gels (6), the use by 3M and Carborundum of the sol-gel process for making oxide fibers (7), and by Dislich and Hussmann (8) at Schott for coating glasses, the Owens-Illinois work on homogeneous glasses (9) and the breakthroughs by Yajima for non-oxide fibers (10) and 3M on abrasive grain (11).

B. Present Conceptual Innovation and Approach

Our conceptual innovation on which the present work rests is, we believe, as major a development as was our development of the sol-gel processing in the decade 1948-58. In that development we succeeded in making ceramics that were homogeneous on the 'unit cell' scale. Since 1982 we conceived and first published and filed patents on and what we have now developed in detail is deliberate heterogeneity on the same scale (10 nm units). The work under this grant is focused on applications and processing, while the thermodynamics and structure of this family of heterogeneous materials is studied under a parallel NSF grant.

C. Results

I. New Diphasic Xerogels

The work in the first year has proved very successful. We have learned the processes to make the following different kinds of diphasic xerogels:

- (a) A SiO_2 or Al_2O_3 gel with extremely fine 1-10 nm crystals of a variety of inorganic crystalline or noncrystalline phases 'precipitated' in the pre-existing host gel [see reprints 1 and 2].

Handwritten notes:
 Further to: Ceramic Composites, Xerogels,
 Sintering, Melting, Nucleation, Epitaxial Growth,
 Chemical Properties, Ultrafine, Microstructure, Colloids,
 Titanium Silica Glass. (56)

- (b) A special case of the former where the 'precipitated' phase is a silver halide--which centers on the whole on a photochromic property [see reprint 3].

II. Diphasic Xerogels for Enhanced Densification and Sintering

Our innovation during the second year of the sol-gel processing work is to use diphasic ceramic xerogels or nano-scale composites as a very general step in processing new ceramic materials. Both compositional heterogeneity and structural 'seeding' have been shown to have profound effects on enhancing densification and sintering. An example of the enormous value of compositional heterogeneity is the use of mixed silica and boehmite sols for the mullite composition instead of the single phase gel. This led to enhanced densification, i.e., 96% density compared to 85%. A typical example of the striking effect of structural heterogeneity is the use of ~1% α - Al_2O_3 seeds in boehmite gels which results in greatly enhanced densification and sintering compared to the unseeded gels (see preprint 1).

III. Microwave Processing of Gels

A systematic though preliminary study of the melting phenomenon of gels in a microwave oven was reported at the American Ceramic Society meeting (see attached preprint 2). Briefly, the very interesting result is that one can melt even a pure Al_2O_3 or SiO_2 gel in a few minutes in a 600 watt home oven. A patent is being applied for with the AFOSR.

During the second year of the program, we have identified new materials which are highly susceptible to microwave radiation and can be used as thermal seeds for microwave processing of gels since the gels do not heat up rapidly in the beginning. A patent application on these materials has been submitted to the AFOSR.

IV. Hydrothermal Processing of Gels

We have defined the process parameters to prepare almost monodispersed, free flowing fine powders in the range of 10-100 nm. Sintering of gels had not been achieved thus far. Sintering of diphasic gels has also been pursued. With their use we seem to be able to control morphology rather well (see manuscript 1).

V. Natural Models

The chemistry and microstructure of a large representative set of naturally occurring single and diphasic gel derived ceramic materials have been investigated in detail in order to understand the mechanism of consolidation at low temperatures. All the materials examined appear to have been formed initially by the random aggregation of 1000-5000Å balls by a sol-gel or solution chemistry process presumably below 100°C (see manuscript 2).

VI. Diphasic Approach to Ultra-Low Expansion (ULE) Glasses

A number of both polar (neoalkoxy and quaternary titanate salts, Ti-ethylene glycol) and nonpolar (Ti-isopropoxides and Ti-ethoxides in ethanol, propanol and chloroform) solvents containing titanium compounds were investigated for gelation of colloidal silica. To date, the best materials were obtained using the Ti-ethylene glycol solution in which the colloidal silica was dispersed and gelled. The sintered materials show a near zero coefficient of thermal expansion (CTE) by dilatometer. Using a differential measurement with 0.5% precision, this material exhibits negative CTE against a commercial silica reference and a slight positive CTE against Corning's ULE glass processed by CVD (see manuscript 3).

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Cumulative List of Publications, Presentations and Manuscripts

Based on This Grant

1. D. Hoffmann, R. Roy, and S. Komarneni, 'Diphasic Ceramic Composites via a Sol-Gel Method,' *Mat. Letters* 2, 245-247 (1984).
2. D. Hoffmann, S. Komarneni, and R. Roy, 'Preparation of a Diphasic Photosensitive Xerogel,' *J. Mat. Sci. Letters* 3, 439-442 (1984).
3. R. Roy, S. Komarneni, and D.M. Roy, 'Multiphasic Ceramic Composites Made by Sol-Gel Technique,' in the Proceedings of the Symposium on 'Better Ceramics Through Chemistry' (Eds. C.J. Brinker et al.), Elsevier, North-Holland, pp. 347-359 (1984) (jointly supported by NSF).
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9. S. Komarneni, R. Roy, E. Breval, and Y. Suwa, 'Hydrothermal Route for Ultrafine Powder Preparation,' *J. Amer. Ceram. Soc.* (in manuscript).
10. R. Roy, Y. Suwa, and S. Komarneni, 'Nucleation and Epitaxial Growth in Reactions of Diphasic (Crystalline + Amorphous) Gels,' presented at the 2nd Intl. Conf. on Ultrastructure Processing of Ceramics, Glasses and Composites in February 1985 (jointly supported by NSF).
11. T.C. Simonton and R. Roy, 'Natural Gel Derived Ceramics: Chemistry, Microstructure and Properties of Opal, Chert, Agate, etc.,' Abstracts of the American Ceramic Society Meeting, Cincinnati, OH, 1985, p. 269.
12. R. Roy, 'Seeding: A Special Approach to Diphasic Xerogels,' Abstracts of the American Ceramic Society Meeting, Cincinnati, OH, 1985, p. 270.

13. R. Roy, 'Microwave Melting of Ceramics and Gels,' Patent application filed via AFOSR.
14. C. Scherer and C. Pantano, 'Ti-Si Glasses Using a Colloidal Sol-Gel Process,' to be presented at the Third International Workshop on Glasses and Glass Ceramics from Gels, Montpellier, France.
15. Y. Suwa, R. Roy and S. Komarneni, 'Crystallographic Effects in Seeded (Diphasic Gels): II. Microstructural and Sintering Properties,' Abstracts of the American Ceramic Society Meeting, Cincinnati, OH, 1985, p. 270.
16. R. Roy, Y. Suwa and S. Komarneni, 'Nucleation and Epitaxial Growth in Reactions of Diphasic (Crystalline + Amorphous) Gels,' in Ultrastructure Processing of Ceramics, Glasses and Composites (Eds. L.L. Hench and D.R. Ulrich), 1985 (in press).

Reprint #1

Multi-Phasic Ceramic Composites Made by Sol-Gel Technique

MULTI-PHASIC CERAMIC COMPOSITES MADE BY SOL-GEL TECHNIQUE

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ABSTRACT

Instead of aiming to prepare homogeneous gels and xerogels, this paper reports on work done to prepare deliberately diphasic materials. This has been achieved by three different paths: (1) mixing 2 sols; (2) mixing 1 sol with 1 solution; and (3) post formation diffusion of either one or two solutions.

By the last named process we have made SiO_2 , mullite and alumina based composites, with silver halides, BaSO_4 , CdS , etc., as the dispersed phase. The crystal size can be confined to the initial pores by rapid diffusion giving rise to extremely fine second phases in the submicron range. Subsequent reduction of appropriate metallic salts can be used to give finely dispersed metals (e.g. Cu, Ni) in essentially any xerogel matrix. The open porosity makes these metal atoms very accessible.

By the first two processes we have made both single phase and di-phasic gels of the same composition (prototype: mullite) and shown that though they cannot be distinguished by XRD, SEM, and TEM, by DTA and thermal processing, they are radically different. Such di-phasic gels store more metastable energy than any other solids.

INTRODUCTION

We developed the sol-gel technique starting in 1948 for two purposes. First, to make ultrahomogeneous glasses and avoid the tedious standard method of the time of making glasses from oxide melts by crushing, re-melting and so on several times. Second, Roy and Osborn had embarked on a low-temperature hydrothermal study of the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ [1], and the glass forming region in the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ was limited to ~0-25% Al_2O_3 . Other starting materials such as silica glass + $\gamma\text{-Al}_2\text{O}_3$ or boehmite reacted to give corundum so early that equilibrium was unattainable. One needed a new method to make noncrystalline phases over a much wider compositional range. Ewell and Insley had already introduced the coprecipitated gels made from Na_2SiO_3 and $\text{Al}(\text{NO}_3)_3$, but even after tedious electrodialysis these always contained substantial (~1%) Na^+ . The use of alkoxide precursors specifically tetraethoxysilane and aluminum isopropoxide proved to be a key to the new generalizable sol-gel process. In the next several years we used the new sol-gel method to make several hundreds of compositions as the homogeneous minimally structurally biased starting materials and making homogeneous glasses [1] for phase equilibrium studies both dry and 'wet', in dozens of binary, ternary and quaternary systems involving all the major ceramic oxides [2-6].

The solution-mixing and sol-gel route was first utilized technologically to make nuclear fuel ceramic pellets by ingeniously shaping the final product while it was a gel at Oak Ridge and Harwell [7]. Scaling up of homogeneous glass making was done at Owens-Illinois [8]. In these studies and in the revival of interest in the sol-gel process consequent

upon the spectacular success of Sowman and colleagues at 3M [9] in making fibers and abrasive grain work has focussed on exactly the same goal: make homogeneous gels, and derive from them, ceramics.

This paper, following the first reports by Roy and Roy [10], describes the reorientation of our original goal of homogeneity on the finest possible scale for the sol-gel method. We set as our new goal the making of new materials with controlled micro- or nano-heterogeneity. The potential value of such di- or more generally, multi-phasic materials is considerable as they allow us to make entirely new families of opto-electro-elastic composites. Further they allow us to make solids which store very large amounts of metastable energy.

EXPERIMENTAL

In the making of any composite we may either make the dispersed phase first (say Al_2O_3 fibers) and build the matrix phase around that (set a gel or melt a glass around the fibers) or one can make the matrix phase and subsequently grow the dispersed phase within it (e.g. all precipitation hardened alloys). In this work we have avoided the first or straightforward method and used either simultaneous creation of the two phases, or the growth of the dispersed phase into a pre-existing matrix.

Opto-Electro-Elastic Composites

1. Materials Studied. Our first objective was to attempt to prepare optically active composites in a dielectric matrix. For the matrix SiO_2 , Al_2O_3 , and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ suggested themselves as the simplest candidates. Dispersed phases suitable for photochromic applications (such as photography) are the silver halides, and for photoreceptor application (such as xerography) include cadmium chalcogenides.

Method Developed

Two methods have been used to make the di-phasic composites. Of those, the one that is relevant to the opto-electro-elastic composites is a two-stage process.

Various silicate or aluminosilicate gels may be used although SiO_2 appears to be the easiest to work with. Tetramethoxysilane (4 parts) dissolved in alcohol (15 parts) and hydrolyzed in water (1 part) at 65°C in 2 cm diameter test tubes. The stiff gel can be removed from the test tubes after drying a little as monoliths. These monoliths are then soaked in the metal nitrate solution for 48 hours. They are removed and washed in distilled water and then soaked in dilute HCl or H_2SO_4 , etc. as desired. By controlling the concentration of the above Cl^- or SO_4^{2-} anions in solution one can form very large numbers of very small nuclei. These di-phasic materials can then be dried at various temperatures or with microwave radiation.

Two classes of di-phasic materials result from this approach, in one both phases are noncrystalline; in the other, one of the phases is crystalline.

Diphasic Ceramic-Ceramic Noncrystalline Xerogels

The second generalized method for making diphasic ceramic xerogels is shown schematically in Fig. 1. The upper portion of the figure represents the normal process of making a homogeneous single phase xerogel and also shows the fact that single phase xerogels may of course (depending on the total composition) yield one, two, or more crystalline phases depending on the phase rule as the composition approaches equilibrium. This is, of

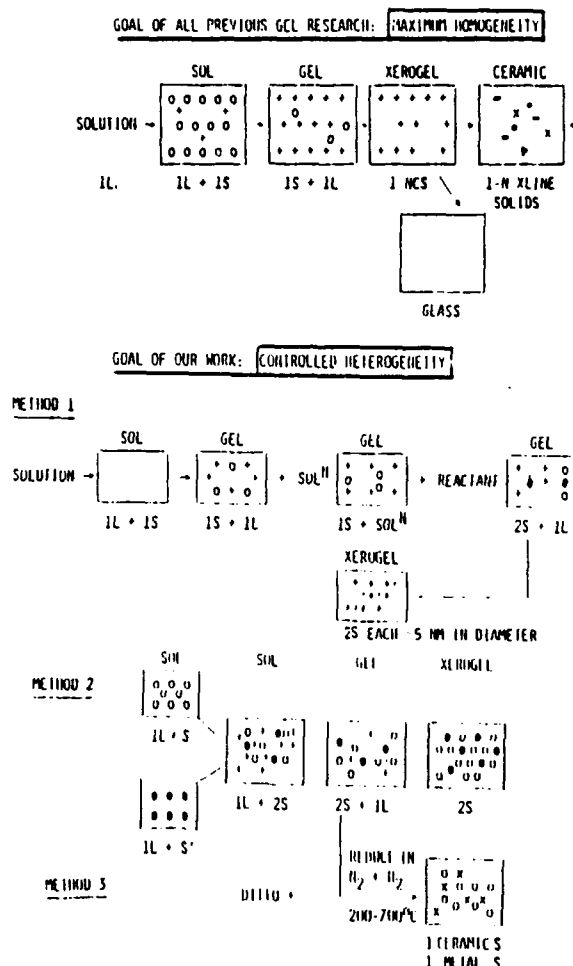


FIG. 1. Stages in the preparation of single phase and di-phasic gels. Three different classes of the latter are illustrated.

course, precisely the way in which such single phase gels were used in our early studies [4] both under dry and hydrothermal condition as the easiest route to the equilibrium crystalline assemblage whether one, two, or multi-phasic.

In the lower portion of Fig. 1 we show two different classes of processes for making diphasic gels. The first is basically mixing two separate sols and gelling the mixture, and the second is dispersing one sol in a solution of a second composition (of one or more components) and then gelling the latter. In the latter case it is difficult to know how much diffusion of the ions of the latter solution may have entered the 'solid' particles of the first sol. The gels are dried by conventional or microwave heating to yield diphasic xerogels.

Diphasic Ceramic-Metal Xerogels

To make ceramic-metal composite materials a third variant is used. We start with either of the following ways for making the xerogel.

1. Method 1. For method 1, in which all components of the xerogel are mixed simultaneously, aluminum nitrate and zirconyl chloride were formed in aqueous, acidic (pH ~1) solution in the case of alumina and zirconia systems. In the case of silica, tetraethoxysilane was dissolved in excess ethanol with an aqueous solution containing the heavy metal ion added simultaneously. The metallic precursor materials were the same for xerogels made by method 1 or 2.

2. Method 2. Pre-made sols containing the constituent oxide component were obtained either as commercial ZrO_2 or $Al(OOH)$ sols; or by hydrolyzing and polymerizing Al-nitrate, tetraethoxysilane or tetraisopropyl orthotitanate. The sols were allowed to sit for various periods of time after being prepared before the heavy metal solution was added.

An additional step of reduction of the diphasic (or monophasic) xerogel product from either of the processes listed above is needed since the xerogel components consist of or contain a relatively easily reducible ion such as Cu, Ni, Co, etc., then the product is reduced usually in a gas phase at 200-700°C usually in N_2+H_2 mixtures, or in solution in contact with the gel. We generate thereby a noncrystalline oxide xerogel matrix which contains probably a crystalline metallic phase, although the units of the latter are so small that we may be approaching noncrystalline metallic phases also.

RESULTS

The different classes of diphasic composites prepared so far are described below together with their structure and properties.

Photosensitive SiO_2 -AgCl, SiO_2 -CdS Materials

Thin layers of the SiO_2 -AgCl diphasic material were prepared by making the gel in a Petri dish, with a range of AgCl concentration from 1-10 mg AgCl per 5 cm³ of gel.

Powder x-ray diffraction shows a crystalline line-broadened AgCl pattern superimposed on a broad amorphous SiO_2 band with samples containing greater than 4% AgCl. Scanning electron microscopy of an opaque sample containing 4% AgCl showed evenly dispersed AgCl crystals of less than one micron diameter. The transparent samples of SiO_2 -AgCl, with lower concentrations of AgCl, contain smaller crystals presumably less than 0.1 micron diameter. Indeed even high resolution TEM studies failed to locate definite AgCl crystals in the low concentration gels (see Fig. 2) suggesting that these are well below 5nm in size.

Infrared absorption spectra of SiO_2 -AgCl samples dried at 60°C, 500°C and 700°C show that the spectrum of the sample dried at only 60°C is identical to that of the sample heated to 500°C. No nitrates or residual organic phases were detected. Absorption bands at 1200, 1120, 800 and 460 cm⁻¹ were observed, which correspond to those typical of silica glass. The band at 950 cm⁻¹ has previously been reported in gel glasses and was attributed to Si-OH vibrations. The band at 3500 cm⁻¹ is attributed to Si-OH stretching and adsorbed water. The 950 and 3500 cm⁻¹ bands were greatly reduced in intensity by heating to 700°C.

During the drying process at 60°C the SiO_2 -AgCl samples shrink considerably, reaching a density of 1.85 g/cm³. Additional heat treatment at

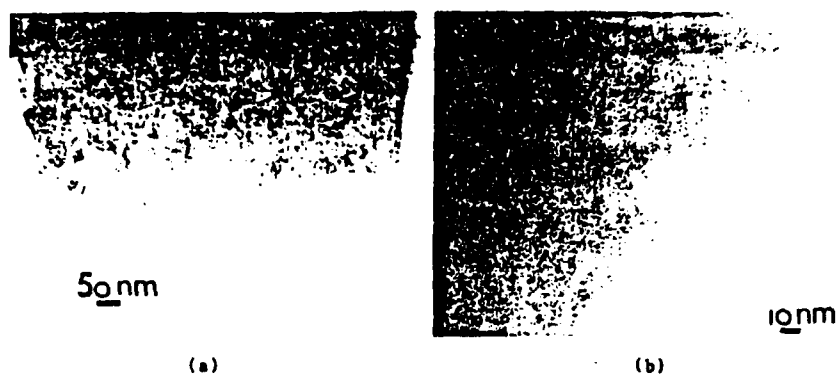


FIG. 2. Nanostructure of AgCl in SiO_2 composites studied by TEM showing that size of AgCl crystals is 5 nm or less.

higher temperatures does not appear to further increase the density.

Samples with greater than 10 mg AgCl per 5 cm^3 silica gel are opaque and white, those with lesser amounts of AgCl are transparent. Upon exposure to sunlight all the materials darken. Samples that were initially transparent remain transparent while darkening, those initially opaque become opaque and black upon exposure to sunlight. The darkening can be almost completely reversed in the samples prepared with 4 mg or less AgNO_3 per 5 cm^3 silica gel depending on the preparation parameters of the present samples (not optimized in any way) by storing them in the dark for hours to days. Heating to 400°C also clears the SiO_2 -AgCl material, which can then be darkened again by re-exposure to sunlight. Examples of such photosensitive SiO_2 -AgCl xerogels are shown in Figs. 3-4.

The addition of the crystalline phase also significantly alters the mechanical properties of the silica gel before densification. For example, gels containing a small amount of AgCl show a much lower tendency

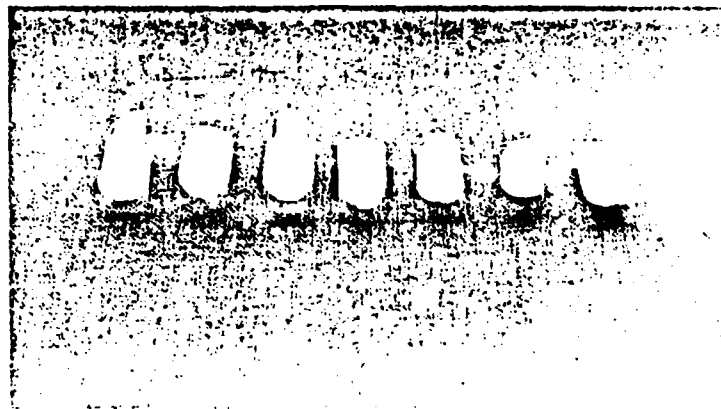


FIG. 3. Samples of SiO_2 -AgCl prepared with 0.4, 1.0, 2.0, 4.0, 10.0, 20.0 and 250 mg of AgNO_3 , respectively, before drying.

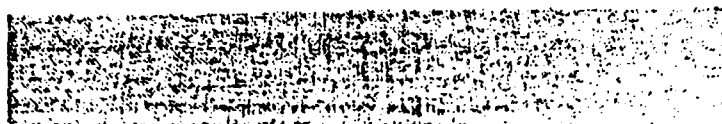


FIG. 4. Same as in Fig. 3 after drying at 60°C and exposing to sunlight.

to crack during densification than pure silica gels. It appears that the introduction of low concentrations of an additional phase may be a useful step in preventing cracking during heat treatment, which is a common problem in the production of monolithic articles via the sol-gel process, the latter being the major focus of much sol-gel research. Details on this study are given elsewhere [11].

SiO₂ Gel Composites with Crystalline CdS, BaSO₄, PbCrO₄

The same method has successfully produced many other nano-composites of 10-50 nm size phases of SiO₂ and another composition [12]. CdS-in-SiO₂ composite thin films have been made using 1N Na₂S₂O₄ at 65°C as the solution for precipitating the CdS. BaSO₄ and PbCrO₄ have also been incorporated as the dispersed phase.

X-ray powder patterns show the presence of crystalline CdS, BaSO₄ and PbCrO₄ in samples with concentrations greater than ~10 mg per 5 cm³ of gel. Photoconductive properties have not been measured yet but it is clear that they can be controlled by controlling the composition (e.g. Se to S ratio) and doping in the crystalline phase, and its concentration. The experimental data are summarized in Table I.

Noncrystalline Diphasic Composites

Table I also lists data on other compositions where the second phase remains noncrystalline as in CaPO₄, AlPO₄, Nd₂O₃ and Ho₂O₃. Whereas in the latter some diffusion of the Nd ions into the SiO₂ may be expected giving gradients in the composition, in the two phosphate examples the two phases should be quite separate. Unfortunately SEM-EDAX fails to resolve the separate compositional areas, which is consistent with our expectation that these are on the order of 10-50 nm.

Comparison of Mullite (3Al₂O₃·2SiO₂) Mono- and Di-Phase Composites

Single phase xerogels had been prepared by dissolving tetraethoxy-silane and aluminum nitrate 9-hydrate in absolute ethanol, then gelling the solution by heating to 60°C in a water bath for several days.

Diphasic xerogels were prepared by different methods. First was by mixing aqueous silica sol (Ludox 'AS,' 2M in SiO₂) with boehmite sol. Opaque gels were formed by reducing the solvent volume by evaporation at room temperature.

TABLE 1. Parameters for Preparation of Diphasic Materials by the Introduction of a Second Phase into 5 cm³ of Silica Gel

Diphasic System	Source of Cation	Source of Anion	Phases Detected IRD
SiO ₂ -CrPO ₄	4.0 mg Cr(NO ₃) ₃ ·6H ₂ O in 25 ml H ₂ O	0.5 M H ₃ PO ₄	NCS
"	40 mg "	"	"
"	400 mg "	"	"
SiO ₂ -BaSO ₄	0.1 mg Ba(NO ₃) ₂ in 25 ml H ₂ O	0.5 M H ₂ SO ₄	BaSO ₄
"	1.0 mg "	"	"
"	10.0 mg "	"	BaSO ₄
"	100 mg "	"	BaSO ₄
SiO ₂ -PbCrO ₄	1000 mg Pb(NO ₃) ₂ in 20 ml H ₂ O	0.5 M chromic acid	PbCrO ₄
SiO ₂ -CePO ₄	500 mg Ce(NO ₃) ₃ in 50 ml H ₂ O	0.5 M H ₃ PO ₄	NCS
SiO ₂ -AlPO ₄	500 mg Al(NO ₃) ₃ ·9H ₂ O in 50 ml H ₂ O	"	NCS
SiO ₂ -Nd ₂ O ₃	1000 mg Nd(NO ₃) ₃ in 25 ml H ₂ O	none used*	NCS
SiO ₂ -Ho ₂ O ₃	200 mg Ho(NO ₃) ₃ in 25 ml H ₂ O	none used*	NCS

*The metal-oxide was formed by heating the samples to 400°C.

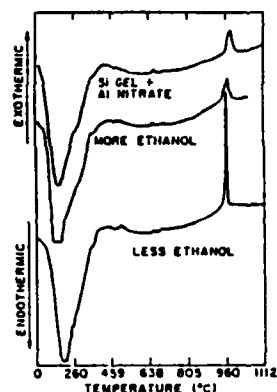
A second method was to disperse a boehmite sol in an alcohol solution of the tetraethoxysilane and causing gelling by heating. A third method was to mix aluminum nitrate solutions with Ludox, with subsequent gelation.

Silica-alumina xerogels were also prepared by immersing a piece of silica gel (formed by the hydrolysis of tetraethoxysilane in ethanol-water) in an aqueous aluminum nitrate solution.

Xerogels were formed by drying the gels in air at 60°C and subsequent heating. The xerogels were ground to powders using an agate mortar and pestle. X-ray diffraction, SEM and electron probe studies showed homogeneous noncrystalline materials with no differences between the single and diphasic materials. DTA curves, however, tell a very different story. Such curves for single phase and diphasic materials are shown in Figs. 5 and 6, respectively.

All of the single phase dried gels exhibit a broad endotherm below 400°C due to the loss of water, ethanol and nitrates. All mullite xerogels show only one sharp crystallization exotherm at 960°C being attributed to mullite crystallization and exactly reminiscent of the transition from metakaolinite to mullite + silica seen on the standard DTA pattern of kaolinite.

FIG. 5. DTA heating curves for single phase xerogels of aluminum to silicon atom ratios 3:1. Bottom: xerogel prepared by gelling 10.2g Al(NO₃)₃·9H₂O and 2 ml TEOS in 10 ml ethanol. Middle: xerogel prepared by gelling 10.2g Al(NO₃)₃·9H₂O and 2 ml TEOS in 30 ml ethanol. Top: xerogel prepared by immersing a TEOS-ethanol gel in 1.5M aluminum nitrate solution for 4 days.



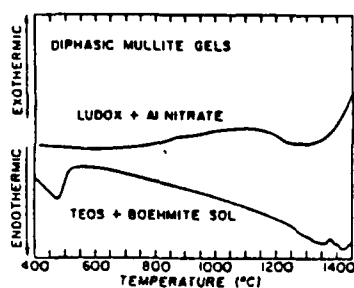


FIG. 6. DTA heating curves for diphasic xerogels of 3:1 Al:Si atom ratio from TEOS-boehmite sol and Ludox-aluminum nitrate.

Figure 5 also shows the effect of preparation conditions on the crystallization exotherms in dried and xerogels having the 'ideal' mullite composition (aluminum to silicon atom ratio 3:1). Parallel to Yoldas' observation on pure Al_2O_3 gels [13], increasing the gel volume changes the

structure of the xerogel sufficiently to be reflected in a much less sharp crystallization exotherm, but does not change its position at all. The enthalpy of crystallization was estimated from the DTA peak area to be on the order of 20 cal/gram (9 kcal/mole mullite) for single phase xerogels of 3:1 aluminum to silicon atom ratio.

DTA of the silica gel immersed in Al-nitrates showed a small, broad crystallization exotherm at 960°C characteristic of a single phase silica-alumina xerogel (Fig. 5), showing that the Al^{3+} ions had penetrated and reacted with the Si-O solid units in the preformed silica gel. However, the homogeneity of the solid units is clearly very different from the best single phase material.

The diphasic xerogels exhibit radically different behavior upon heating from single phase xerogels of the same stoichiometric composition. DTA heating curves for diphasic xerogels are shown in Fig. 6. The endotherm at 400°C is associated with the decomposition of the boehmite phase. No trace of the 960°C exotherm seen in single phase xerogels was observed. Instead a very broad exotherm associated with mullite formation occurs over the entire region from about 700 to above 1250°C. X-ray powder diffraction data on diphasic gels made from Al_2O_3 -sols shows the presence of a discrete boehmite phase at low temperatures. Cristobalite crystallization precedes mullite formation when the gels are heated, confirming the fact that the two discrete phases are reacting 'independently' up to ~1000°C.

The diphasic xerogels prepared by gelling tetraethoxysilane with boehmite sol, and by gelling Ludox and aluminum nitrate provide the most interesting data. The latter is not complicated by the boehmite dehydration and shows no trace of the mullite formation exotherm at 960°C. Instead there is apparently continuous reaction over a several hundred degree range, with a much larger total ΔH of reaction which is, however, very difficult to quantify.

Samples of both single phase and diphasic xerogels were subjected to ultrafast heating on a platinum strip furnace, by presetting the temperature to the desired level, turning off the furnace, placing the pinhead size sample on the strip and switching on the current. No metastable melting of the mullite composition was observable (as direct slumping) below 1750°C.

Ceramic-Metal Diphasic Xerogel Composites

Details of our work have recently been published [14] and only a summary is presented here. Some compositions studied are listed in Table II.

Table III lists typical process conditions for making a ceramic-metal xerogel. While the exact details of the process 'recipe' vary substan-

tially over the wide range of cermet systems studied. Table III shows that all materials were initially gelled at or below 70°C. In general, when gelation was allowed to occur in an open system, it took place in times ranging from several minutes to several hours. In closed systems (no H₂O evaporation during gelation), the time ranged from 1/2 hour to several days.

Drying and heat treatment took place after the wet gel formed was found to have sufficient rigidity. The final step was to place the sample in a furnace and react with a reducing atmosphere of 'forming gas' (95% N₂, 5% H₂) temperature was varied for different samples ranging from 200°-700°C. Typical treatment times ranged from 15 to 40 minutes.

In all the systems (except TiO₂-Cu) listed above we obtain composite xerogel materials consisting of a nanocrystalline oxide matrix which is itself either the pure original oxide or slightly doped with the metal oxide, and a finely dispersed metal phase. The nanostructure of the gel and the metal phases is shown in SEM and TEM photographs in Figs. 7 and 9 and XRD data in Fig. 8.

In sum, what these data show is that the xerogel itself is typically made up of 50 nm globules aggregated into larger 500-1000 nm globular clusters of oxide. Dispersed among these globules are metal particles ranging in size from 5nm at 400°C in the case of Pt on Al₂O₃ increasing to about 30nm at 700°C.

Figures 7 and 9 show SEM and TEM micrographs of a 10% Pt/Al₂O₃ xerogel prepared at 500°C. The pores visible as light areas in the TEM micrograph are the same size as the agglomerated particles visible in the SEM micrograph. In addition, small Pt crystallites about 10-15 nm appear as dark spots. In Fig. 9 a TEM micrograph of the xerogel 10% Pt/Al₂O₃ is compared with a sputtered film of a similar composition. Both materials contain Pt crystallites about 10 nm in size, although the sputtered film

TABLE II. Ceramic-Metal Systems Studied.

Alumina:	Cu, Pt, Ni
Zirconia:	Cu, Ni
Silica:	Cu, Sn
Titania:	Cu

Starting Materials	
Oxides	
Al ₂ O ₃	- Al-nitrate, Al-isopropoxide, AlOOH sols
ZrO ₂	- Zirconyl chloride, ZrO ₂ sols
SiO ₂	- SiO ₄ , tetraethoxy (or methoxy) silane
TiO ₂	- Tetraisopropyl orthotitanate
Metals	
Cu	- Cu-nitrate, Cu-sulphate, Cu-chloride
Pt	- H ₂ PtCl ₆
Sn	- SnCl ₂ ·2H ₂ O
Ni	- Ni-nitrate, Ni-sulphate

TABLE III. Typical Process Conditions.

Gelation	
temperature	- RT-70°C
pH	- <1.5
system	- open or closed
Drying	
a)	ambient several hours --> days
b)	oven 110°-125°C, 30 minutes
c)	microwave
d)	reducing furnace 200°-700°C, 10 minutes

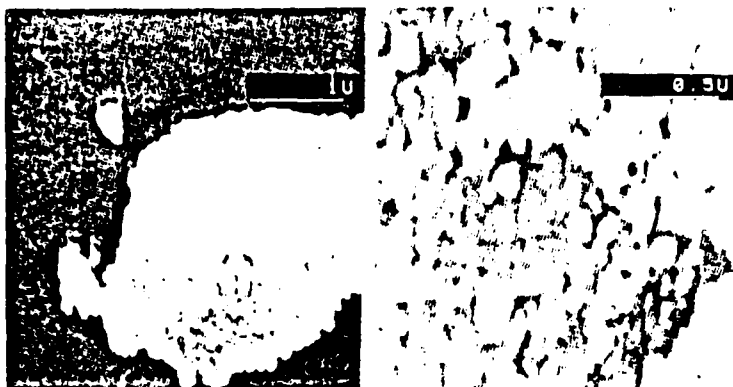


FIG. 7. SEM micrographs of a 10% Pt/ Al_2O_3 xerogel at two different magnifications.

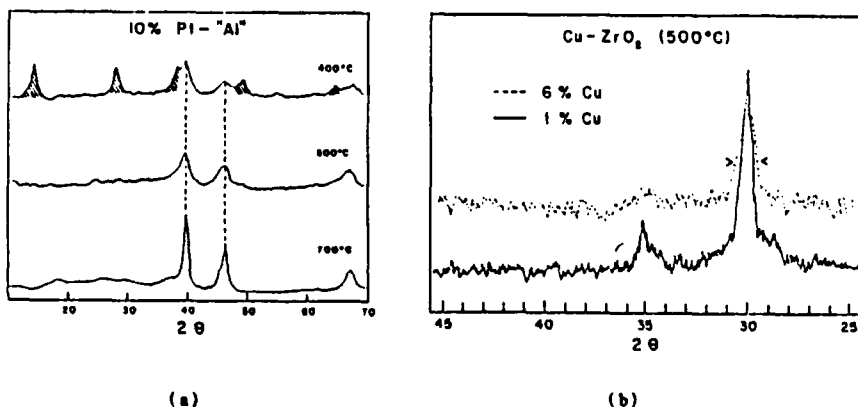


FIG. 8. XRD patterns of (a) 10% Pt/alumina gels as a function of reduction temperature. The dotted lines indicate the position of platinum peaks. (b) Cu/zirconia gels as a function of % Cu.

is less porous. In addition, the Pt crystallite size in the porous oxide matrix can be varied by heat treatment in the gel, as noted previously. In xerogels of Cu-in SiO_2 , or Cu in ZrO_2 , more of the copper stays in the oxide host, whether NCS as in the case of SiO_2 or poorly crystalline as in the case of ZrO_2 . The radical difference between such diphasic xerogel ceramic-metal composites (before they are compacted by hot pressing or HIPing) and other materials is in their enormous accessible surface area.

This unique porosity in the xerogels was evident in a series of experiments with Ni- Al_2O_3 and Cu- Al_2O_3 diphasic materials. Some of these composites when reduced at 500°C - 700°C were black due to the presence of a metallic phase, although this was not always detectable by x-ray diffraction. However, after exposure to room temperature ambients for periods from 15 minutes to one week, the metal is reoxidized and a green or blue xerogel obtained.

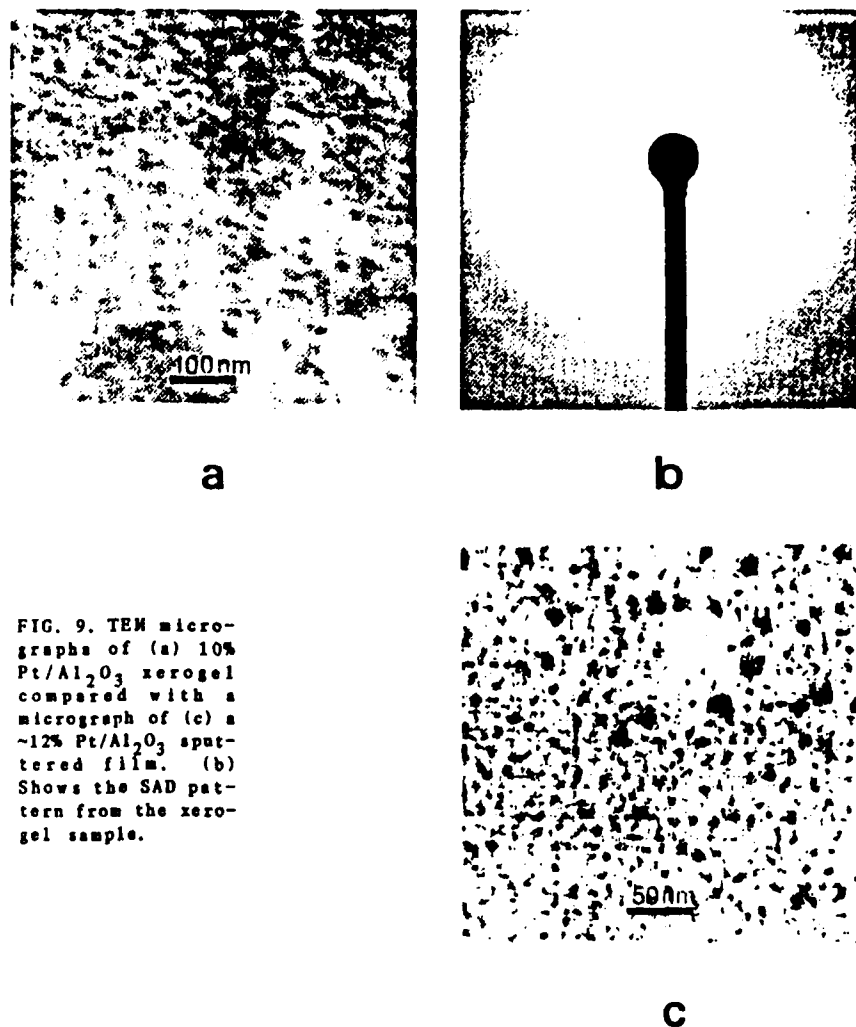


FIG. 9. TEM micrographs of (a) 10% Pt/Al₂O₃ xerogel compared with a micrograph of (c) a ~12% Pt/Al₂O₃ sputtered film. (b) Shows the SAD pattern from the xerogel sample.

The G-T diagram of Fig. 10 explains the theory of the actual application of each of the three mechanisms in materials processing. Metastable assemblages of any kind whether caused by surface energy or noncrystallinity MUST melt at a temperature below the equilibrium melting point. By that token diphasic xerogels, if metastable equilibrium could be attained, will melt far below the equilibrium T_m . However, equilibrium (metastable or stable) is not always attained. Indeed in the 'glass-forming' oxide materials we are discussing, below about 1000°C equilibrium is extremely difficult to attain at all and the reactions which occur are determined by the kinetics. In the regime between 1000-2000°C the roles of kinetics and equilibria are more equal in the typical experiments which run from

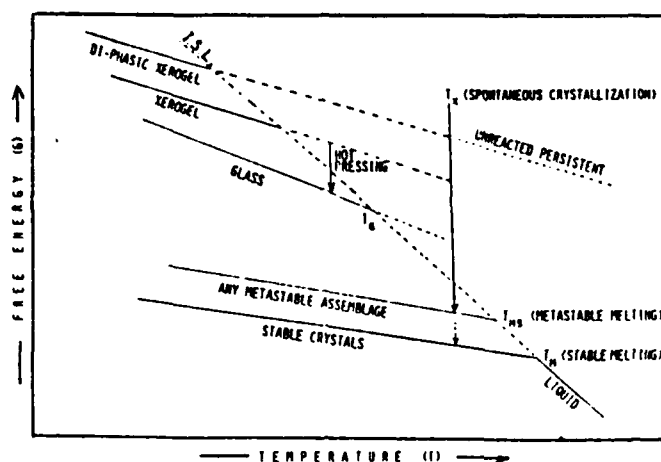


FIG. 10. Schematic G-T diagram for an isoplethal system to illustrate the variety of different reactions which can be encountered in heating meta-stable phases including xerogels.

minutes to days, so that one can expect to observe some of the phenomena represented schematically in Fig. 10. Other phenomena encountered include non-nucleated crystallization shown as occurring at T_s . For mullite containing compositions this seems to be $\sim 960^\circ\text{C}$; above this temperature no NCS solid of the mullite composition can exist since it crystallizes spontaneously and very rapidly. This is why we have been unable to observe the metastable melting point of a xerogel in the Al_2O_3 - SiO_2 system.

SUMMARY AND DISCUSSION

The preparation of di- or multiphase xerogels has opened the way to making really new classes of materials at temperatures below 600 – 700°C .

1. Noncrystalline oxide xerogels containing as a second phase very small 5 – 50 nm crystals of a wide assortment of inorganic phases such as AgCl , CdS , BaSO_4 , etc.

2. Noncrystalline or poorly crystalline oxide xerogels containing as a second phase very small 5 – 100 nm crystals of a wide assortment of metals Cu , Ni , Pt , etc.

3. Two noncrystalline oxide phases each of which is 5 nm or less in size. In such materials there are 3 sources of excess free energy over the stable equilibrium state

- (a) the excess surface energy of such small particles,
- (b) the difference between the stable crystalline state and the noncrystalline state,
- (c) the heat of reaction of the two phases to the stable assemblage.

Since the two phases can be very far from equilibrium with each other, they can store via (c) above in a solid far more energy than is possible by the other means (a) and (b). Typically (a) and (b) will be at most 1 – 3 kcal/mole of simple oxides, whereas (c) can be one order of magnitude more.

However, in the $\text{Al}_2\text{O}_3\text{-MgO}$ system in which the 3M abrasive grains are made [9], it is likely that all or part of the gel actually melts metastably near 1250°C in order for the reported sintering to be accomplished at that temperature.

ACKNOWLEDGEMENTS

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Reprint #2

Diphasic Ceramic Composites Via a Sol-Gel Method

DIPHASIC CERAMIC COMPOSITES VIA A SOL-GEL METHOD

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A sol-gel process is described for the preparation of diphasic composite materials. The method involves the growth of extremely fine crystalline or non-crystalline materials inside a pre-made gel structure (of SiO_2) by soaking the gel in metal nitrate solution and subsequent precipitation of the metal with the selected anions (using mineral acids) followed by a densification step.

1. Introduction

Our early work following the invention of the alkoxide-based sol-gel process by one of us [1,2] led to the preparation of an enormous compositional range of ceramic *powders*. Recent work, often oblivious of the extensive early work, has often repeated this attempt at compositional diversity. Thus Gonzales-Oliver et al. [3] reported in 1982 the preparation of SiO_2 - TiO_2 glasses which DeVries et al. [4] reported in 1954 as simply another application of a routinely used preparation technique.

The ceramic xerogel powders prepared in our early (1948-60) studies were *multi-component* but *single* phases and almost universally non-crystalline. Occasionally the gels processed at 1 atm or under hydrothermal conditions typically at 1000-2000 atm, adventitiously formed roughly equant monoliths from a few mm to 1 cm in size. Recent work in this area has focused almost exclusively on the preparation of ultra-homogeneous single-phase "large" glassy xerogel monoliths, e.g. those of nearly pure SiO_2 [5-7]. However, it is obvious that the single-phase xerogel in the complex compositions studied say, for example, in MgO - Al_2O_3 - SiO_2 - H_2O [8] would on heat treatment and equilibration yield polyphasic ceramics. This is, for instance, true of the major technological sol-gel success so far, i.e. the 3M abrasive grain [9], the xerogel of which yields Al_2O_3 and spinel phases.

This study forms part of a new initiative to make a new class of composite solids - diphasic xerogels. Thus Roy and Roy [10] first reported the preparation of this class of solids in which two ceramic sol derived gel phases are intermixed on a scale of $\approx 100 \text{ \AA}$ leading to a ceramic-ceramic composite, or one where one of the phases could be reduced to give a metal-ceramic composite. The present paper provides for the first time details on still another method to create diphasic ceramic matrix composites where one of the phases may be a very finely divided crystalline phase, such as a sulphate or chromate. Such a sol-gel route presents a vastly more versatile - with respect to composition of the matrix - approach to such two-phase materials than is possible with say, precipitation out of a glass. Of course, the latter has been successfully utilized for generations in opacified and opal glasses and more recently in photochromic glasses [11]. Our materials could, on the one hand, extend the processing options with respect to the latter, and on the other hand allow us to make alternative gel bases for the organic materials used in ordinary photography.

2. Experiments

Silica gels were prepared by mixing ethanol, tetramethoxysilane and water in the ratio 15 : 4 : 1 by volume. The clear solution was poured into $15 \times 2 \text{ cm}$

test tubes, which were covered and placed in a water bath at 65°C for 24 to 48 h until a clear, stiff gel was formed. The gels were allowed to dry at room temperature until just enough shrinkage had occurred for the gel to slide from the test tube.

The metal cation desired in the second phase was introduced by placing the silica gel in a beaker containing aqueous metal-nitrate solution [$\text{Ba}(\text{NO}_3)_2$, for example]. Initially, the gel floats but soon sinks as the ethanol in the gel pores exchanges with the aqueous metal-nitrate solution.

After 48 h the metal-nitrate solution was drained and the gel was rinsed with deionized water, and then placed in an aqueous solution of the anion component of the desired second phase (H_2SO_4 solution for example). By controlling the concentration of the solution, small crystals of the insoluble second phase rapidly form inside the pores of the gel.

The new "diphasic" ceramic composite was dried at 60°C for 48 h, and in some cases was then given a second heat treatment at higher temperatures. A summary of diphasic materials prepared is given in table 1.

3. Results and discussion

Data on diphasic composites, prepared by precipitating a second phase within silica gel, are summarized in table 1. Powder X-ray diffraction was used to iden-

tify crystalline barite and lead chromate in the SiO_2 - BaSO_4 and SiO_2 - PbCrO_4 , respectively. No crystalline phase was detected by X-ray diffraction in samples of SiO_2 - AlPO_4 , SiO_2 - CePO_4 , SiO_2 - CrPO_4 , SiO_2 - Nd_2O_3 and SiO_2 - Ho_2O_3 . The SiO_2 - CrPO_4 is transparent green, presumably due to hydrated chromium phosphate. The SiO_2 - Nd_2O_3 and SiO_2 - Ho_2O_3 have the characteristic color of the metal oxides. The SiO_2 - AlPO_4 is colorless. These are true diphasic xerogel composites.

Crystal growth within gels is an old technique for obtaining large, high-quality single crystals using extremely low growth rates [12] on very few nuclei. The process described in this paper is a modification of this old technique, where rapid crystal formation is used to obtain very small, evenly distributed crystals within the silica gel. The method has not, to our knowledge, previously been exploited as a means of preparing composite materials with the dispersed phase being on the submicron scale.

The size of the crystals formed within the silica gel is probably influenced by the concentration of cation present before the crystalline phase forms. Evidence for this is provided by the transparent and opaque SiO_2 - AgCl materials produced using different concentrations of AgNO_3 reported earlier by us [13]. Further studies using transmission electron microscopy are underway to substantiate this hypothesis. The silica gel microstructure (pore size) is probably correlated

Table 1

Parameters for preparation of diphasic materials by the introduction of a second phase into 5 cm³ of silica gel

Diphasic system	Source of cation	Source of anion
SiO_2 - CrPO_4	4.0 mg $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 25 ml H_2O	0.5 M H_3PO_4
SiO_2 - CrPO_4	40 mg $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 25 ml H_2O	0.5 M H_3PO_4
SiO_2 - CrPO_4	400 mg $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 25 ml H_2O	0.5 M H_3PO_4
SiO_2 - BaSO_4	0.1 mg $\text{Ba}(\text{NO}_3)_2$ in 25 ml H_2O	0.5 M H_2SO_4
SiO_2 - BaSO_4	1.0 mg $\text{Ba}(\text{NO}_3)_2$ in 25 ml H_2O	0.5 M H_2SO_4
SiO_2 - BaSO_4	10.0 mg $\text{Ba}(\text{NO}_3)_2$ in 25 ml H_2O	0.5 M H_2SO_4
SiO_2 - BaSO_4	100 mg $\text{Ba}(\text{NO}_3)_2$ in 25 ml H_2O	0.5 M H_2SO_4
SiO_2 - PbCrO_4	1000 mg $\text{Pb}(\text{NO}_3)_2$ in 20 ml H_2O	0.5 M chromic acid
SiO_2 - CePO_4	500 mg $\text{Ce}(\text{NO}_3)_3$ in 50 ml H_2O	0.5 M H_3PO_4
SiO_2 - AlPO_4	500 mg $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 50 ml H_2O	0.5 M H_3PO_4
SiO_2 - Nd_2O_3	1000 mg $\text{Nd}(\text{NO}_3)_3$ in 25 ml H_2O	none used ^{a)}
SiO_2 - Ho_2O_3	200 mg $\text{Ho}(\text{NO}_3)_3$ in 25 ml H_2O	none used ^{a)}

^{a)} The metal-oxide was formed by heating the samples to 400°C.

with the size of the crystals formed within the gel. Since the gel microstructure and gel formation time can be controlled by altering the ratio of alkoxysilane to alcohol and water [14], it should be possible to control the size and distribution of the crystalline phase by manipulation of these variables.

The addition of the second phase significantly alters the properties of the silica gel before densification. For example, gels containing a small amount of AgCl show a much lower tendency to crack during densification than pure silica gels [13]. The introduction of low concentrations of an additional phase may be a useful step in preventing cracking during heat treatment, which is a common problem in the production of monolithic articles via the sol-gel process.

4. Conclusions

Novel ceramic matrix composites can be produced by a sol-gel process introduced in this work. The size and distribution of a crystalline or non-crystalline dispersed phase within the matrix gel can be controlled by this process. A major advantage of this process is the low temperature at which high-melting-point (and non-melting) materials can be incorporated into a non-crystalline xerogel matrix, which may of course be melted to a glass.

Acknowledgement

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Reprint #3

Preparation of a Diphasic Photosensitive Xerogel

Preparation of a diphasic photosensitive xerogel

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From the time of the discovery by one of us [1] in the early fifties of the sol-gel method using organic precursors for preparing glasses [2] and ceramics the key advantages of the method have been purity and homogeneity of compositional distribution on the finest scale. The recent revival of interest in the sol-gel process, consequent upon the finding by Leitheiser and Sowman [3] of its value in abrasive grain technology reflects this same focus: making a homogeneous gel. In the hundreds of papers presented at international conferences held during the last few years only two papers report on the deliberate attempt to make inhomogeneous gels and xerogels. In these papers by Roy and Roy [4, 5] we have set out the principles of the different ways in which two phase gels can be made. In the light of the interest in ceramic-ceramic composites this method offers novel possibilities for combining two different phases on a very fine scale. In this study we report on the successful preparation of such a composite of a photosensitive halide in a high temperature oxide gel. The need for an inorganic base for photographic processes is now confined to speciality products but may one day be much larger. In addition to the advantage of a low processing temperature, the gel method of preparation introduces additional processing variables which can be easily exploited to control the silver halide crystal size and spatial distribution.

Although more complex compositions such as mullite also work we report here only on pure

SiO₂ gels. Silica gels were prepared by mixing ethanol, tetramethoxysilane and water in the ratio 15:4:1 by volume. The clear solution was poured into 15 x 2 cm test tubes, which were covered and placed in a water bath at 65°C for 24 to 48 h until a clear, stiff gel was formed. The gels were allowed to dry at room temperature until just enough shrinkage had occurred for the gel to slide from the test tube.

The silver cation was introduced by placing the silica gel in a beaker containing aqueous silver nitrate solution. Initially, the gel floats, but soon sinks as the ethanol in the gel pores exchanges with the aqueous silver nitrate solution. After 48 h the silver nitrate solution was drained and the gel was rinsed with deionized water, and then placed in an aqueous hydrochloric acid solution. Very fine insoluble silver chloride crystals rapidly formed inside the pores of the silica gel as the Cl⁻ ions diffuse rapidly through the gel. The "diphasic" material was dried at 60°C for 48 h, and in some cases was then given additional heat treatment at higher temperatures. A summary of materials prepared with different AgCl concentrations is given in Table I.

Thin, transparent pieces of SiO₂-AgCl were prepared by gelling a shallow solution of tetramethoxysilane in a petri dish or beaker. The same treatments with AgNO₃ and HCl solutions were used to form the crystalline AgCl phase in the thin silica gel.

The materials prepared were characterized by

TABLE I Parameters for the introduction of a second phase into 5 cm³ of silica gel

Diphasic system	Source of cation	Source of anion
SiO ₂ -AgCl	0.4 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	1.0 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	2.0 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	4.0 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	10 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	20 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl
SiO ₂ -AgCl	250 mg AgNO ₃ in 25 ml H ₂ O	0.5 M HCl

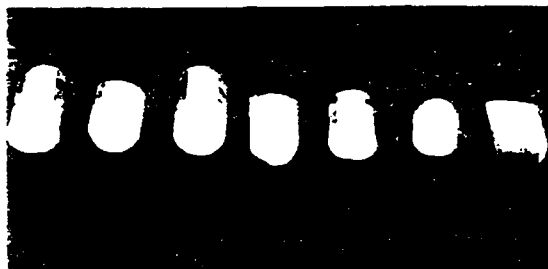


Figure 1 Samples of $\text{SiO}_2\text{-AgCl}$ prepared with 0.4, 1.0, 2.0, 4.0, 10.0, 20.0 and 250 mg of AgNO_3 , respectively, before drying.

X-ray diffraction, SEM and IR spectroscopy. The latter was carried out using a Perkin-Elmer PE 283 B double beam spectrometer, and dispersing the $\text{SiO}_2\text{-AgCl}$ samples in KBr pellets.

Diphasic $\text{SiO}_2\text{-AgCl}$ xerogels were prepared with a range of AgCl concentrations. Samples with greater than 10 mg AgCl per 5 cm^3 silica gel are opaque and white, those with lesser amounts of AgCl are transparent. Upon exposure to sunlight all the materials darken. Samples that were initially transparent remain transparent while darkening, those initially opaque become opaque and black upon exposure to sunlight. The darkening can be almost completely reversed in the samples prepared with 4 mg or less AgNO_3 per 5 cm^3 silica gel depending on the preparation parameters of the present samples (not optimized in any way) by storing them in the dark for hours to days. Heating to 400°C also clears the $\text{SiO}_2\text{-AgCl}$ material, which can then be darkened again by re-exposure to sunlight. Examples of the photosensitive $\text{SiO}_2\text{-AgCl}$ are shown in Figs. 1 to 4.



Figure 2 Same as in Fig. 1 after drying at 60°C and exposing to sunlight.



Figure 3 Transparent pieces of $\text{SiO}_2\text{-AgCl}$.

Powder X-ray diffraction shows a crystalline line-broadened AgCl pattern superimposed on a broad amorphous SiO_2 band. Scanning electron microscopy of an opaque sample containing 4% AgCl showed evenly dispersed AgCl crystals of less than one micron diameter. The transparent samples of $\text{SiO}_2\text{-AgCl}$, with lower concentrations of AgCl, contain smaller crystals presumably less than $0.1\text{ }\mu\text{m}$ diameter.

Infrared absorption spectra of $\text{SiO}_2\text{-AgCl}$ samples dried at 60 , 500 and 700°C are shown in Fig. 5. The spectrum of the sample dried at only 60°C is identical to that of the sample heated to 500°C . No nitrates or residual organic phases were detected. Absorption bands at 1200 , 1120 , 800 and 460 cm^{-1} were observed, which correspond to those typical of silica glass. The band at 950 cm^{-1} has previously been reported in gel glasses [6] and was attributed to Si-OH vibrations. The band at 3500 cm^{-1} is attributed to Si-OH stretching and adsorbed water. The 950 and 3500 cm^{-1} bands



Figure 4 Same as in Fig. 3 after exposure to sunlight.

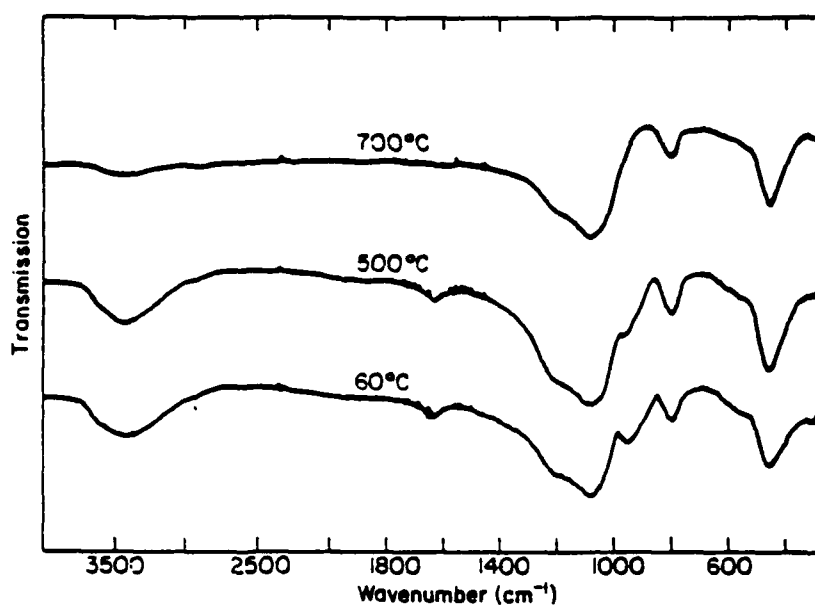


Figure 5 Infrared spectra of $\text{SiO}_2\text{-AgCl}$ samples dried at different temperatures.

were greatly reduced in intensity by heating to 700°C .

During the drying process at 60°C the $\text{SiO}_2\text{-AgCl}$ samples shrink considerably, reaching a density of 1.85 g cm^{-3} . Additional heat treatment at higher temperatures does not appear to further increase the density.

Growth of large crystals within gels is an old technique for obtaining high quality single crystals using slow growth rates, (see for example the review in [7]). The process described in this paper is the direct opposite of this old technique. Instead of using very slow diffusion to grow on the very few nuclei, we use rapid nuclei formation to obtain a large number of very small, evenly distributed crystals within the silica gel. The method is quite general and we have prepared a variety of such ceramic-ceramic composites containing BaSO_4 , CdS , etc., as the dispersed phase. The method has not to our knowledge previously been exploited as a means of processing diphasic ceramic composite materials.

The size of the silver halide crystals formed within the silica gel can be influenced by the concentration of cation present before the crystalline phase forms. Evidence for this is provided by the transparent and opaque $\text{SiO}_2\text{-AgCl}$ materials produced using different concentrations of AgNO_3 . It is also likely that there is a correlation between the silica gel microstructure (pore size) and the size of the crystals formed within the gel. It is plausible that the largest crystals which can form

are those which contain the amount of cation present within a single gel pore. Since the gel microstructure and gel formation time can be controlled by altering the ratio of alkoxysilane to alcohol and water [8], it should be possible to control the size and distribution of the crystalline phase by manipulation of these variables. Similarly by incorporating appropriate habit modifiers in the gel or solution it may also be possible to control the morphology of the dispersed phase.

The protons in silica gel are only weakly acidic [9]. This suggests that the silver cations introduced into the silica gel are not bound to the gel surface, but instead remain in aqueous solution in the gel pores until the chloride anion is introduced and the crystalline phase precipitated.

The addition of the crystalline phase significantly alters the mechanical properties of the silica gel before densification. For example, gels containing a small amount of AgCl show a much lower tendency to crack during densification than pure silica gels. It appears that the introduction of low concentrations of an additional phase may be a useful step in preventing cracking during heat treatment, which is a common problem in the production of monolithic articles via the sol-gel process, the latter being the major focus of much sol-gel research [10].

The variation of the diphasic xerogel process introduced in this work is a novel method of producing photosensitive materials. Advantages of this process which can easily be exploited are the large

number of processing variables which can be manipulated, allowing the size and distribution of the crystalline phase within the silica to be controlled, and the low temperature at which the photosensitive composite material can be produced.

Acknowledgement

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Preprint #1

Controlled Microwave Sintering and Melting of Gels

CONTROLLED MICROWAVE HEATING AND MELTING OF GELS

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Abstract

Controlled microwave heating and melting of silica, alumina and aluminosilicate gels were achieved in a 600 watt domestic-type oven. The microwave absorption mechanism of these gels is not yet clear. However, we have been able to define the parameters whereby rapid heating (including melting) is achieved for silica, alumina and aluminosilicate gels. Empirical results indicate that the heating behavior is dependent on the chemistry, structure, and mass of the gels.

Introduction

The use of microwave radiation in ceramic processing covers a very diverse set of purposes. Figure 1 clusters these uses into five sets. In order to set the present work in perspective we differentiate the others from our own.

1. The first category we label 'process control' where microwave radiation is used as a measurement or monitor of process parameters such as moisture content, thickness, large flow density, etc. (see Campbell and Shivers¹).
2. A second category is, the best known use of microwaves, for drying ceramic ware. This has a very long history going back at least to the early postwar years (see Von Hippel²). The water molecule's rotational modes absorb in the 1-2 GHz region; this forms the basis for all home cooking and drying of any articles containing water.
3. A third category is perhaps the newest of the applications. It is the use of microwave plasmas to assist in the decomposition of gaseous species and produces highly excited electronic states of the elements that recombine to give metastable phases. The work by Kamo et al.³ on diamond synthesis falls into this category.
4. A fourth category of research which has received much recent attention⁴ by Johnson and Rizzo is the use of a microwave-plasma assist in the sintering of oxides. This is distinct from the category 3, in that no vapor phase material is converted to the solid.
5. The fifth category is the one in which the present work falls. It is absorption of microwave energy by solid ceramics as a source of internal heating. There are two completely distinct families of

materials to which this can apply. The first is the only one which appears to be understood and which has been utilized in commerce. Ferrimagnetic insulators such as ferrites absorb microwaves due to the eddy current losses, and hence sintering of ferrites can be accomplished in the clean non-contact environment of a microwave cavity, see Krage⁵.

This paper is concerned with certain observations of absorption of microwave radiation in pure, simple oxide ceramics. Such reports have been appearing with increasing frequency during the last year or two. Normally of course, ceramic materials as a class are regarded as transparent in the microwave region, but our own work and the papers we will cite show that this is far from true for all ceramic materials.

Our interest in the field was stimulated by the paper by Haas⁶ who reported that UO_3 could be melted in a home microwave oven. We were unable to repeat this observation, even though we used various stoichiometries of crystalline solutions, which we thought were the key to the absorption. Two other observations were significant in stimulating our interest. The first was the accidental, nearly explosive heating up and breakage of a Corning 'Centura'-ware cup in a home oven. The second was the accidental melting at 1400°C of a 100 ml beaker full of a gel of complex aluminosilicate composition in the same 600 watt oven.

In 1982, the literature on the solid-state heating to sintering temperature and melting of non-magnetic ceramics was virtually non-existent. There was no clear theory as to the possible mechanisms with the exception of a study on $\beta\text{-Al}_2\text{O}_3$ ⁷. We therefore undertook a preliminary, empirical study of the phenomena involved in the microwave heating of simple oxide gels; this paper presents the results of that study. Since this work was essentially completed, two papers have appeared in this area, one by McDowell⁸ reporting

on possible reasons for the Corning Centura ware phenomenon, and the other by Quemener⁹ on the clinkering of current compositions in a microwave cavity.

Experimental

Compositions Studied

Experiments were conducted with alumina, silica and mullite gels; sintered alumina and mullite were also studied for comparison with the gels. Alumina gel was prepared by acidifying boehmite sols (Dispural) in water. Twenty g of Dispural in 50 ml deionized water was treated with ten drops of conc. HCl; this sets to a firm $\text{AlO} \cdot \text{OH} \cdot \text{H}_2\text{O}$ gel in about 20 minutes. Silica gel was prepared by mixing ethanol, tetraethoxysilane and water in a 15:4:1 volume ratio and gelling at 65°C for four days in a water bath. Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ gel was made by dissolving $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol mixing with tetraethoxysilane and gelling at 65°C for two days in a water bath. Sintered alumina and mullite samples obtained from commercial source* were used.

Experimental Arrangement

Microwave heating of samples was conducted in a 600-W, 2.45 GHz commercial home microwave oven with a 13-in. wide x 13-3/4-in. deep x 7-1/8-in. high cavity containing an insulated 'chamber'. The sample was placed inside a cell made of a zirconia insulating cylinder with zirconia boards at the bottom and top of the cylinder. The top board has a hole in the middle for inserting a Pt/Pt, 10 Rh thermocouple which is covered with platinum foil to prevent microwave absorption by the thermocouple ceramic shield. The thermocouple was connected to a digital display from the back of the oven to read the temperature. The zirconia cell was surrounded on all sides by 2-3

*McDanel Refractory, Beaver Falls, PA.

inches of fiberfrax insulation. The temperature was recorded every five seconds as the heating progressed in the microwave oven.

The phases formed by microwave heating and the starting materials were characterized by powder x-ray diffraction (XRD) using a Philips APD 3600 x-ray diffractometer.

Results

Gels

The temperature attained at or near the gel surface in the microwave oven is plotted against time for alumina gel (Figs. 2 and 3). These plots all show a characteristic pattern: the temperature increases slowly for a period of time (of some 5-15 minutes), when there is a sudden very rapid increase in temperature which is also sustained for a long time. We designate the time where there is a sudden increase in rate of temperature rise in the gel as the triggering time. After considerable time it was realized that this triggering time as well as the heating rate seem to be a function of gel weight. This can be seen in Figs. 2 and 3. Figures 4, 5 and 6 show more clearly the results of experiments designed to determine the effect of gel weight on the triggering times for alumina, silica and mullite gels, respectively. These results show that the triggering time decreased with an increase in gel weight up to an optimum gel weight after which the triggering time reached a steady state for a while and then seemed to decrease with an increase in gel weight upon exposure to the microwaves with the configuration used in these experiments. This trend is most obvious with the silica gel. At the optimum weight, the triggering time for the three gels decreased as follows: alumina gel < silica gel < mullite gel.

Figures 7, 8 and 9 depict the effect of gel weight on peak heating rates for alumina, silica and mullite gels, respectively. These results also show

that the heating rate remained steady up to a critical weight and then increased suddenly. For masses above this critical mass, the peak heating rate seemed to reach a steady state using the particular insulating configuration.

The data also establish that the peak heating rate was also a function of the composition of the gel. At the optimum weight, the peak heating rates were arranged as follows:

alumina gel > silica gel > mullite gel.

The temperatures were recorded with a Pt-Rh thermocouple up to 1500°C and then the microwave oven was turned off. These temperature measurements were quite accurate, unlike the earlier studies^{8,10} where approximate temperatures were measured. X-ray diffraction analysis of the alumina, mullite and silica gels heated to 1500°C revealed the crystallization of corundum and mullite in the former two while silica remained amorphous. When melting of the gels was the objective, the thermocouple was removed and the microwave heating was continued for about ten minutes. Silica gel could be melted in the present configuration but not alumina or mullite gels. Porous, very low density silica was obtained by melting the silica gel.

Sintered Alumina and Mullite in Microwave Cavities

In order to test the role of the water and the detailed microstructure of the gel, the heating of the gels was compared with the microwave absorption and heating of sintered materials such as alumina and mullite. The Al_2O_3 did in fact heat substantially, the mullite much less so. The average peak heating rates of sintered alumina and mullite were 16° and 6°C/sec. respectively, while that of the insulated chamber itself was 8°/sec. (Fig. 10). It will be seen that these peak heating rates of sintered alumina and mullite, were much lower than those of the respective gels (Figs. 7 and 9).

Since it was to be expected that the dielectric loss at 2.45 GHz would increase with temperature¹¹, and a certain minimum absorption rate would be necessary to allow the 'runaway' condition to start, experiments were conducted with preheated sintered alumina and mullite.

The triggering times for such preheated sintered alumina and mullite were determined for different temperatures and are shown in Fig. 11. The results show, as expected, that the higher the initial temperature, the shorter is the triggering time.

Discussion

What has been established in this study is that a 'critical mass' of a gel of pure SiO_2 , Al_2O_3 , and at least some silicates could be heated to between 1500-1750°C in a few minutes in a 600 watt 2.45 GHz home oven. The mass required is in the order of 10-20 gms. There is definitely some chemical composition dependence of the microwave absorption since Al_2O_3 , SiO_2 , and mullite gels behave very differently. Studies of sintered alumina and mullite materials in comparison with gels of same composition show that structure of material clearly makes a marked difference in triggering rapid heating and the peak heating rate. In these materials (e.g., SiO_2) the loss mechanism is far from clear. It is impossible to speculate at this stage on the precise relaxation mechanism for the microwave radiation absorption by these gels since there is no information on the dielectric properties of gels. We hope to measure the absorption spectra of gels with a 10 MHz-100 GHz spectrometer which will be set up in our laboratory in the very near future and then it will be possible to decipher the mechanism. In these gels, there is no sodium ion to be responsible for the loss by rattling in a cage which has been suggested as the mechanism for the high microwave susceptibility of pure sodium nepheline⁸. The role of the size and shape of the sample in relation

to the wavelength at 2.45 GHz has yet to be studied. Also, the role of microstructure of each gel which is dependent upon various process parameters¹² also needs to be investigated. Such detailed studies are underway.

Conclusions

It has been demonstrated that alumina, silica and mullite gels could be heated rapidly to very high temperatures in a 600 watt kitchen oven with proper insulation. In fact, silica gel was melted under the present experimental conditions. Studies are presently underway to unravel the mechanism for the high susceptibility of the gels to microwave radiation. With the emergence of sol-gel technology in the ceramic industry, the high susceptibility of gels to microwave radiation gives an excellent processing option.

Acknowledgement

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Figure Captions

- Fig. 1. Use of microwave radiation in ceramic processing.
- Fig. 2. Dependence of temperature on microwave heating time for 6g alumina gel.
- Fig. 3. Dependence of temperature on microwave heating time for 14g alumina gel.
- Fig. 4. Dependence of triggering (sudden rise in temperature) time on alumina gel weight.
- Fig. 5. Dependence of triggering time on silica gel weight.
- Fig. 6. Dependence of triggering time on mullite gel weight.
- Fig. 7. Peak heating rate plotted against alumina gel weight.
- Fig. 8. Peak heating rate plotted against silica gel weight.
- Fig. 9. Peak heating rate plotted against mullite gel weight.
- Fig. 10. Peak heating rate vs. preheating temperature for sintered alumina, sintered mullite, and insulated chamber.
- Fig. 11. Dependence of triggering time on preheating temperature for sintered mullite and sintered alumina.

Microwaves and Ceramics

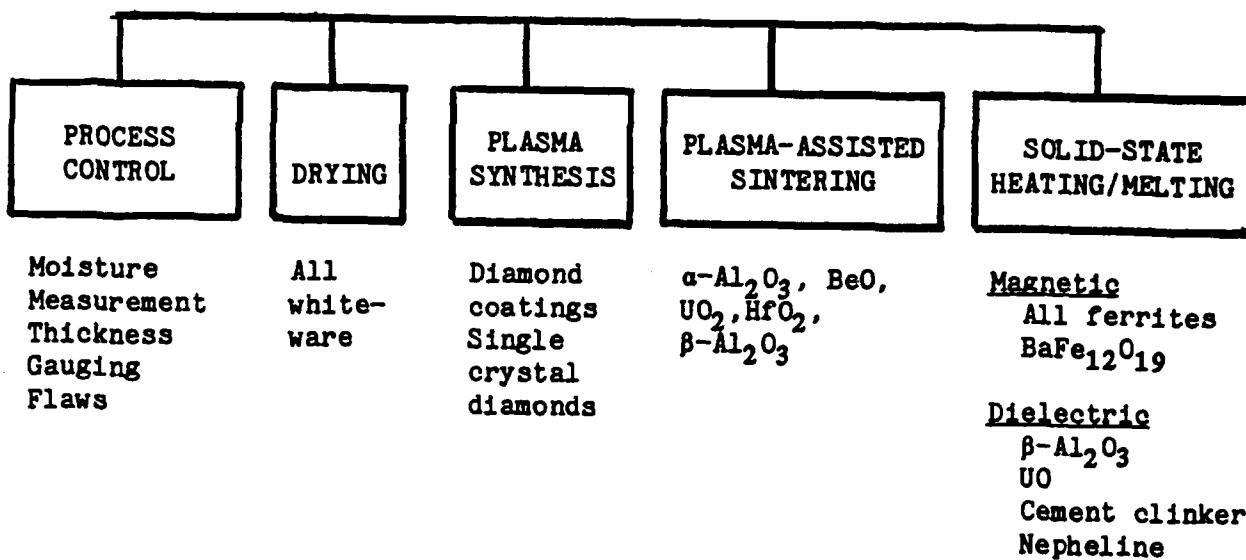


Fig. 1

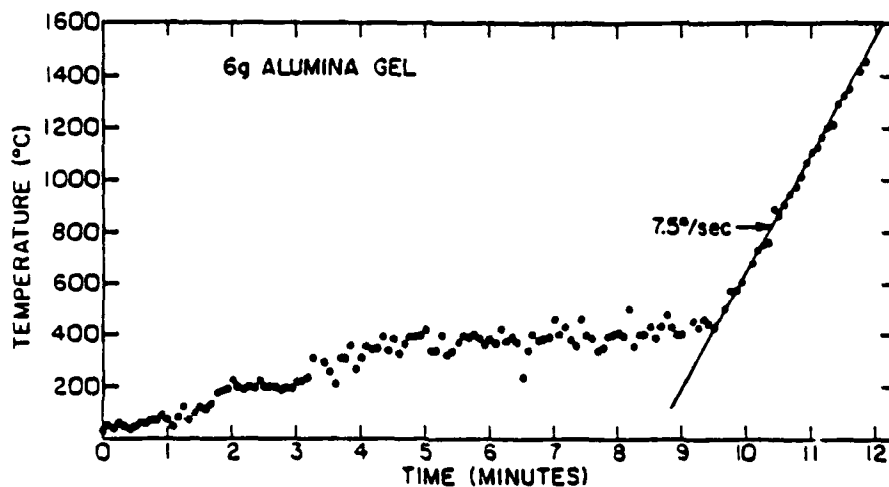


Fig. 2

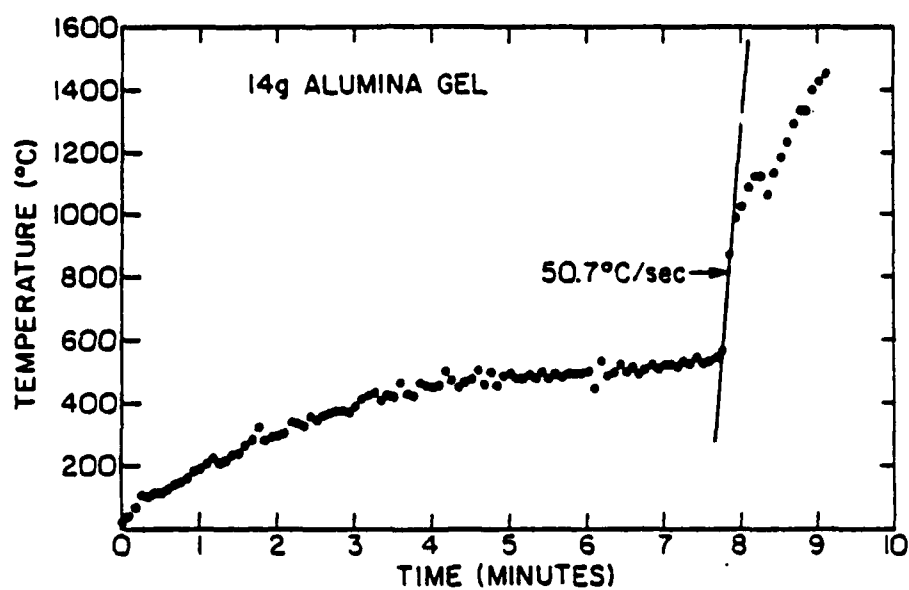


Fig. 3

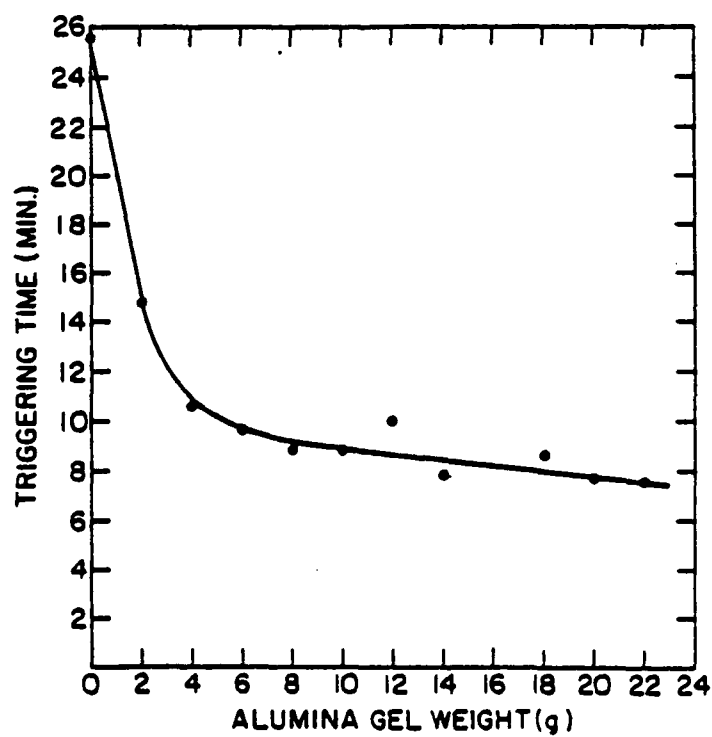


Fig. 4

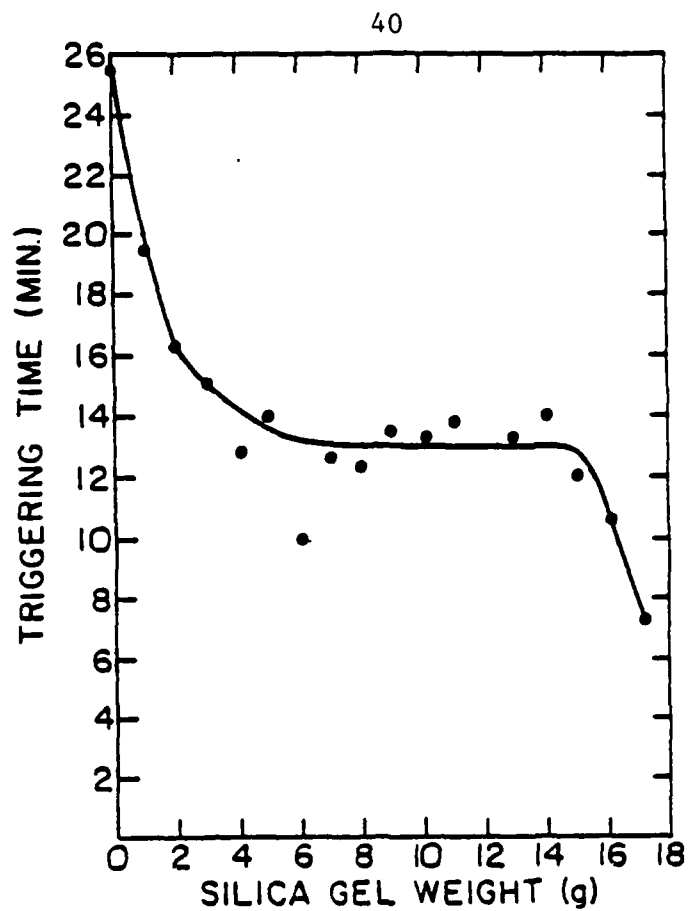


Fig. 5

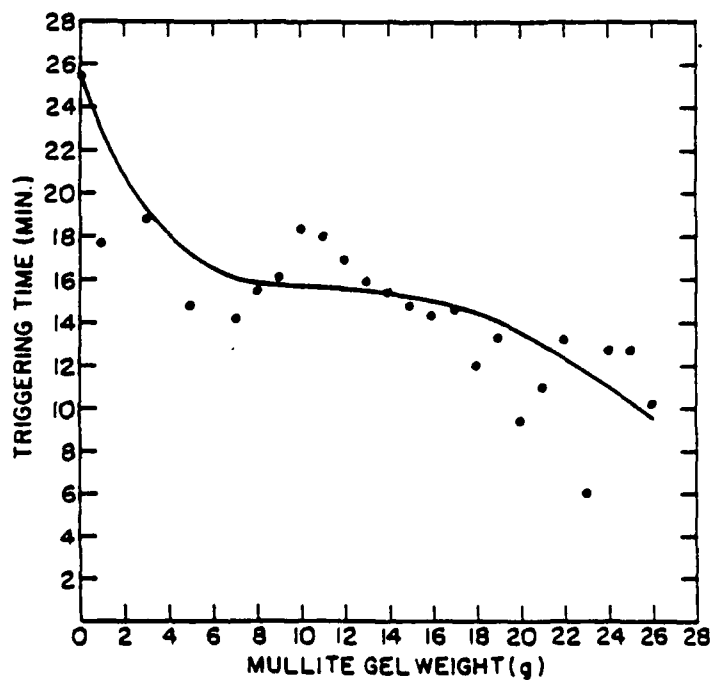


Fig. 6

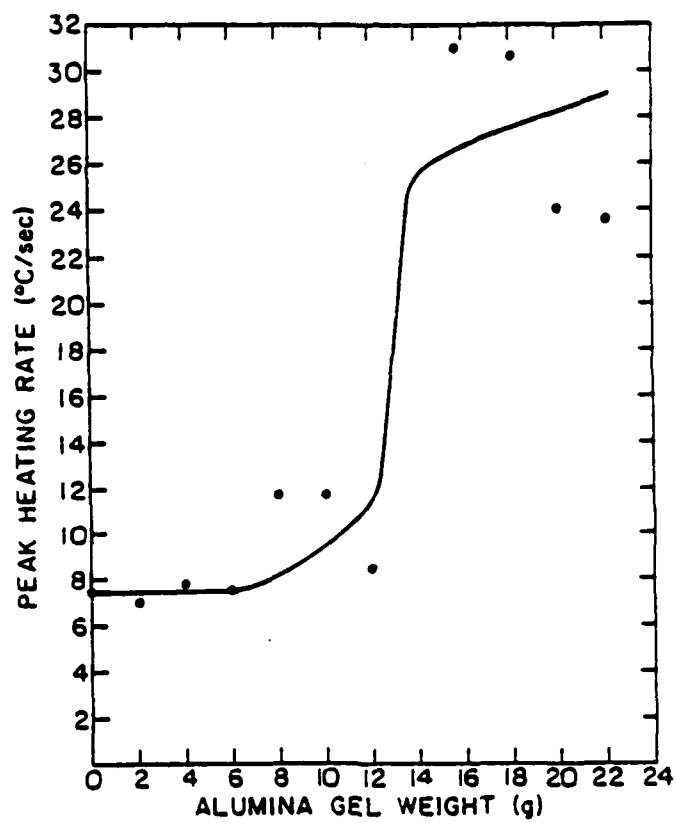


Fig. 7

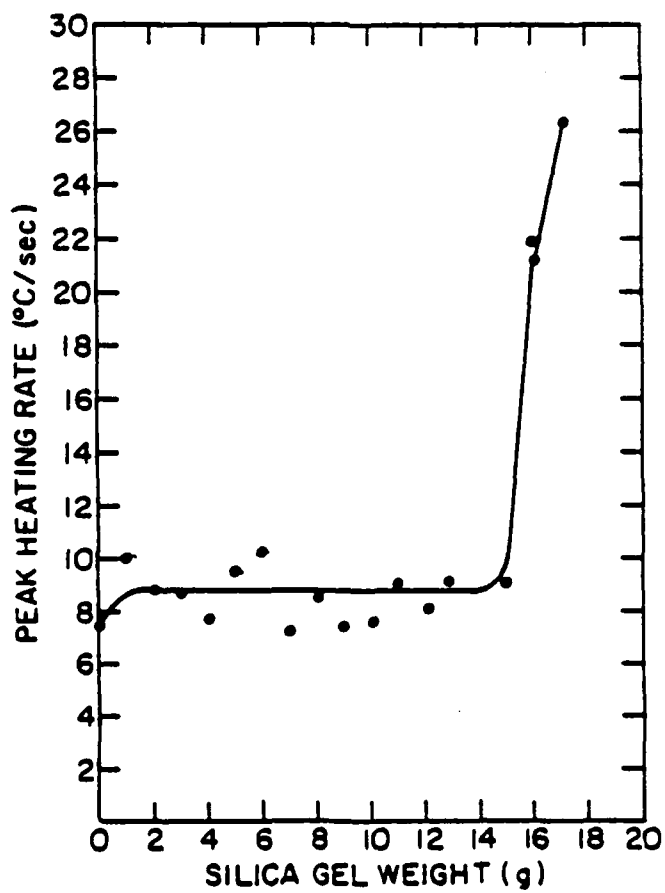


Fig. 8

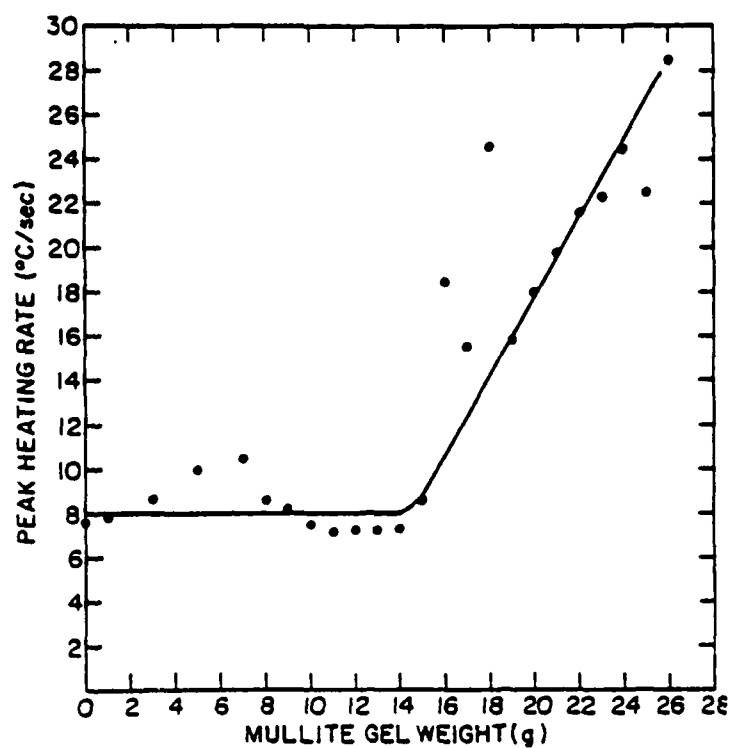


Fig. 9

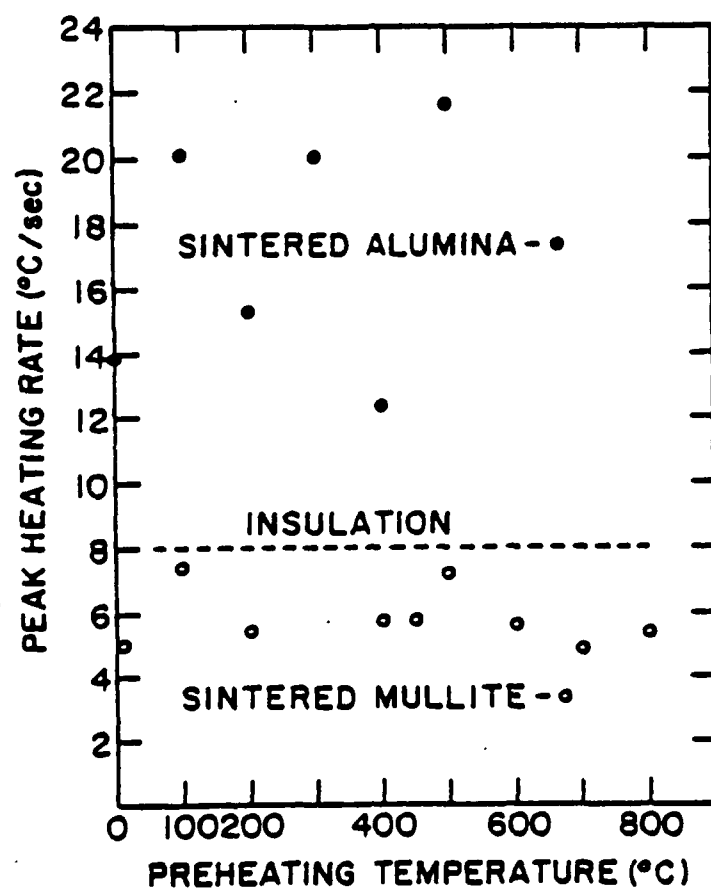


Fig. 10

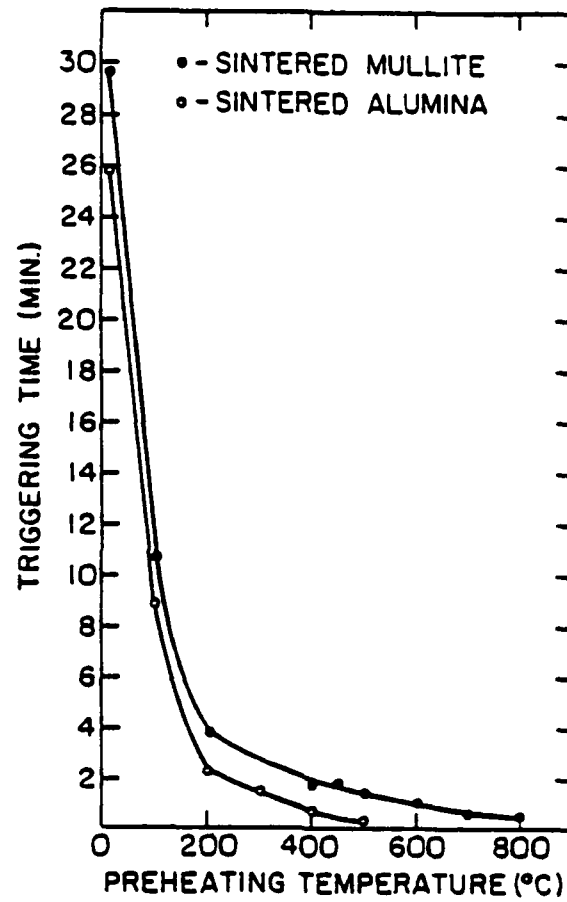


Fig. 11

Preprint #2

Nucleation and Epitaxial Growth
in Diphasic (Crystalline + Amorphous) Gels

NUCLEATION AND EPITAXIAL GROWTH IN DIPHASIC (CRYSTALLINE + AMORPHOUS) GELS

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1. INTRODUCTION

1.1 SG, The Route to Homogeneous Ceramics

The sol-gel (SG) process as a route to homogeneous ceramics and glasses was conceived, demonstrated and applied in some thousands of ceramic compositions by the senior author and his colleagues and students starting in July 1948. In the decade following we reduced to routine practice the mixing in solution (starting with both inorganic and organic precursors many of which were rare chemicals in those days) and thence the formation of sols, and then gels and xerogels. We covered all the most common ceramic oxide compositions (involving Al, Si, Ti, Zr, etc.) (1-5) in both simple and one-component and complex up to 5- and 6-component systems. This discovery of making ultrahomogeneous oxide solids via the SG route instead of the oxide powder mixing route became widespread in the community of experimental geochemists and petrologists. Literally hundreds of papers were published employing our sol-gel method to make homogeneous multi-component oxide compositions. Nearly two decades elapsed before the ceramics community became aware of its potential and then only in the industrial research laboratories.

Technologically, till the mid-sixties these papers stimulated very little interest. The catalyst industry (e.g., the Filtrol Corporation, which had supported some of our work) used aluminosilicate gels extensively, and Dupont where the pioneering work of R.K. Iler on sols was done and the, then, new silica sol products under the trade name 'Ludox' developed, were exceptions.

Between 1965 and 1980 the pace of research in industry on technological applications of the sol-gel process was intensified in a few corporations and

new products were successfully introduced or partially developed and abandoned:

1. Nuclear fuel pellets at Oak Ridge (6).
2. Ceramic fibres by 3M and Carborundum (7), including non-oxide fibers (8).
3. Abrasive grain by 3M (9).
4. Glass melting research done on a small pot-scale by Bausch and Lomb was extended to full tank scale in a very substantial development effort by Owens-Illinois (10). But this was terminated just before the oil price shock, just when its energy-conserving advantage might have helped.
5. Two obvious areas of applications: large area thick (1 mil. +) coatings and bulk ceramics received considerable industrial attention, but they had not been successfully translated into major products. The more recent successful work of Yoldas (11) in the coatings area showed not only that one could make excellent coatings from organic precursors, but also that these could not be made very thick ($>>1\mu\text{m}$).

We regarded the various products with satisfaction as the much delayed technological developments based in general on the 'science' of the fifties of solution mixing and subsequent gelation and firing. What is relevant to this paper is the fact that the products of the science, and of all these technologies, were maximally homogeneous ceramics and glasses. The recent voluminous literature on sol-gel structures and processes which has accumulated in the last four or five years is likewise exclusively devoted to the same goal--homogeneous materials.

1.2 The New Direction: Maximally Heterogeneous Nanocomposites

In 1982 the senior author first reported (12) that the sol-gel route used by everybody (including himself) exclusively to make such maximally homogeneous ceramic materials, could be turned around to make maximally (i.e., in the degree of interpenetration of phases), heterogeneous materials. Under

this rubric we have now demonstrated a wide range of possibilities of using the sol-gel route for making this wholly new class of materials which we call 'nanoscale composites' derived from 'di (or multi) phasic xerogels.'

A nanoscale composite (including the di-phasic xerogel) is a material which has two (or more) phases with the physical dimensions of the phases lying in the range 1nm to 10nm. The two phases may differ in either composition or structure or both. Thus we can have a nanocomposite of 10nm SiO_2 and 10nm Al_2O_3 particles, or 10nm AlOOH and 2.5nm AgCl , or 10nm rutile crystals + 100nm noncrystalline TiO_2 , or 10nm AlOOH + 20nm $\alpha\text{-Al}_2\text{O}_3$. The significance of some members of this class of nanocomposite materials is just beginning to be appreciated. In the metals area Gleiter and Marquardt (13) for instance title their 1984 paper 'Nanokristalline Strukturen ein Weg zu neuen Materialien,' Schechtman, Blech, Gratias and Cahn (14), and Levine and Steinhardt (15) in very recent papers in Phys. Rev. Letters (November 1984 and to be published, 1985) show for example, that in certain rapidly quenched alloys ($\text{Al}_{86}\text{Mn}_{14}$) one observes extraordinary crystallographic structures or quasi-crystals with the five-fold icosahedral symmetry disallowed to crystals with large sizes and translational symmetry. We had already approached the making of such very finely heterogeneous material from the vapor phase by co-sputtering of ceramics + ceramics, ceramics + metals and ceramics + polymers some years ago in this laboratory. The papers by Messier, Roy (R.A.) and Cowley, and Roy (R.A.) and Cowley (16,17) described for example the extraordinary structure of the $\sim 2\text{nm}$ gold crystals dispersed in a Al_2O_3 matrix. However, both the methods referred to in the referenced papers--the very recent rapid solidification of a melt or earlier co-sputtering--have severe limitations on compositional flexibility, volume of samples, etc. The success of the current series of experiments summarized in this paper is in the synthesis of an array of these new materials--nanoscale composites--via the

sol-gel route. This method provides an enormous flexibility with respect to variation of composition and structure, and metastable energy storage combined with relative ease of preparation, for the making of nanoscale composites and products derived therefrom.

1.3 Epitaxial Growth in S-V, S-L and S-S Systems

During the development of the SG process we had reasoned that the ideal method required a true ionic or molecular single phase solution of all the components, so that homogeneity was guaranteed in the smallest possible volume. Where we could change the solution to a solid by change of some intensive variable without permitting fractionation we had achieved our goal. As we found that use of 10-100nm SiO_2 -sols (Ludox) or Al_2O_3 -sols appeared to make hardly any difference in the FINAL product after firing to make glasses or ceramics, it became clear that at these highest temperatures and the longest times differences in homogeneity (in the original gel) between 0.5nm and 5 or 50nm were obliterated by diffusion and reaction in these times. But at lower temperatures or shorter times the di-phasicity made a great difference.

We have already noted that the two phases in a nanocomposite or a diphasic xerogel may differ in composition or in structure, and the possibilities of using structurally diphasic materials at low temperatures was worth exploring. The concept of 'seeding' by providing a lower activation energy path to the nucleation of the thermodynamically (more) stable phase is well known. Perhaps the best known example is the hetero-homo* epitaxy of H_2O -ice on AgI seeds during vapor-solid condensation. Even in the L-→S--melt solidification--cases however, epitaxial effects except in garnet and semiconductor technology have not been studied in great detail, although they

*The first descriptor refers to the composition, the second to the structure. Thus, Si on Si is homo-homo epitaxy while BN on diamond is hetero-homo, and NH_4I on mica is hetero-hetero.

are often assumed to exist. Only recently Fang and Roy (18) attempted to quantify the lattice mismatch required for hetero-hetero epitaxial growth of ADP, and TGS on mica. Simple ratios of lattice mismatch were shown to be insufficient guides. We have very little work in the case of pure S→S epitaxy, i.e., overgrowth of a crystalline phase by solid phase reaction in the presence of an epitaxial substrate, we have not found any literature. In a manner of speaking, various topotactic reactions (19) in complex silicates may be thought of as a self-seeded epitaxy, where one part of the structure provides a persisting structural element which controls the formation of the final product. Martensitic phase transitions may also be treated as examples of solid phase epitaxy (20) in this limited sense.

As we embarked on our new emphasis of studying the science of heterogeneous or diphasic gels the role of seeding in the sol-gel process became important. Two radically different mechanisms are to be distinguished. The first is the mutual interaction of charged colloidal particles and the possible resulting mutual orientation of the two particles. From the classical work of Biltz summarized by Zsigmondy in 1905 and 1925 (21,22) one notes that 'protective colloids' have a particular relation to each other. Figure 1 illustrates Zsigmondy's picture of the specific 'protection' of a Au sol particle by gelatine particles, with a reversal of phases occurring when the ratio of sizes is reversed. Such mutual interactions which are at least (in part) controlled by the charge on the particles can only occur in mixed sols of relatively low viscosity. While the role of the charge on the particle is clear, what is less clear is whether the structure of the solid phase can cause a specific mutual orientation between particles.

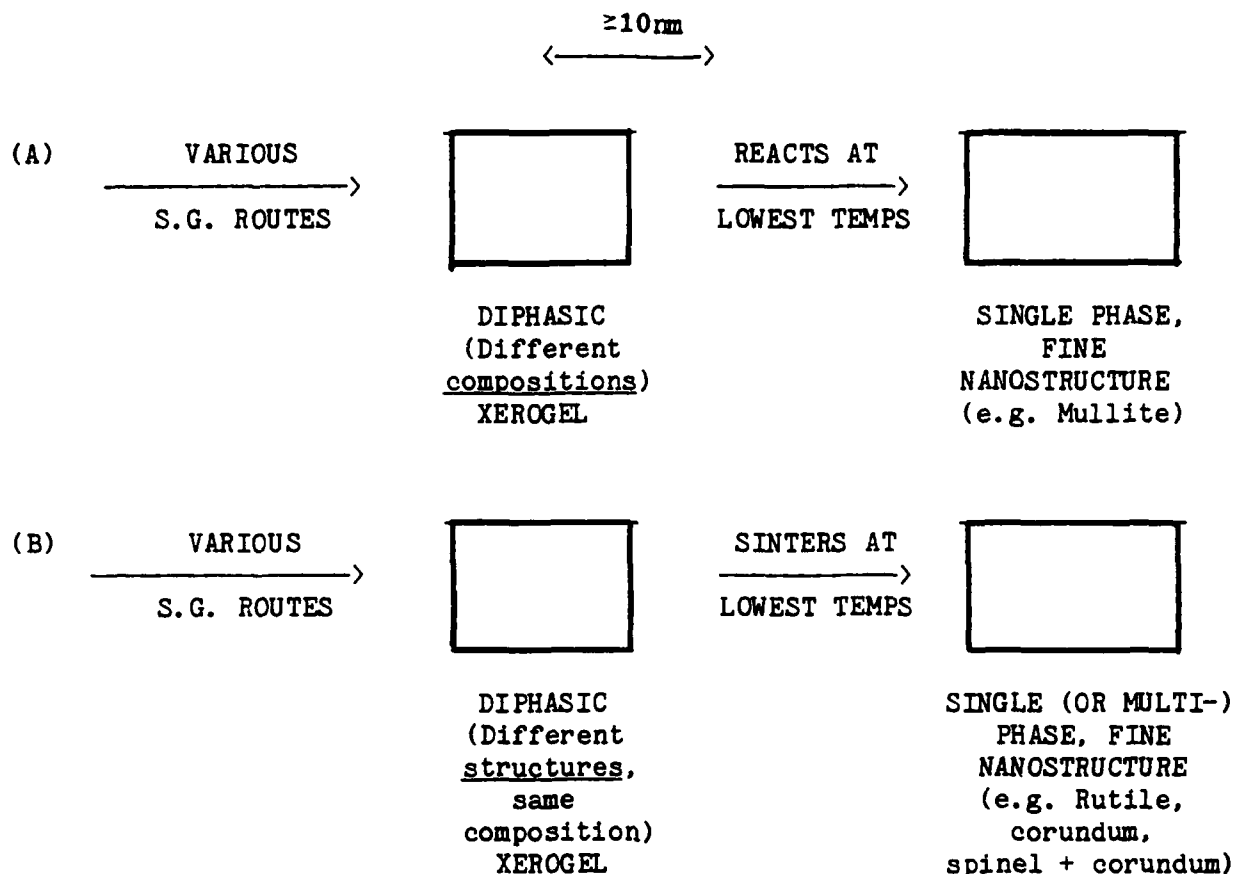
That crystal 'structure' plays some role is evident from the well known technique of 'decorating' clay particles with colloidal gold. Here the diphasic sol on dehydration results in a solid with gold particles being

adsorbed on the edges of the dominantly hexagonal clay platelets (23).

Our purposes in the work on the diphasic xerogel regime were very different. It was to catalyze reactions to attain equilibrium within the final solid assemblage most easily. Thus very early (1949) in our studies with gels, in order to get reaction at the lowest temperatures we introduced the practice of seeding of gels with the same structure as we expected in the final product. Indeed it was found that the phase diasporite (AlOOH) could not even be formed without diasporite seeds in an alumina gel (24). We were later able to over-ride this requirement of seeds by using higher pressure and no seeds (25). Similar results were obtained with α -spodumene and many geochemical workers adopted the practice of seeding gels to catalyze the crystallization of the phase expected to be at equilibrium under the p,t conditions of reaction (26). The mechanism for the efficacy of such seeding was assumed to be by transport of Al and oxygen ions via the solution phase. The final element of our previous SG research that was relevant to our conceptualization of the present nanocomposites was our research on crystal growth in gels. For instance, in McCauley and Roy's work (27) on the formation of CaCO_3 crystals in SiO_2 gel it was possible to control the structure of the crystalline phase (whether calcite, aragonite or vaterite) by adjustment of ion activities. In this work we were able to actually demonstrate the epitaxial control of the final phase (i.e., aragonite growing on Sr or Mg-rich seeds, by finding the original nucleus inside the final crystal and analyzing it in the electron microprobe. In this case of course, although the gel network is critically controlling the diffusion, we are dealing with a L→S crystallization reaction.

Thus our present experiments have been designed to demonstrate the use of the SG route to make two classes of diphasic xerogel ceramic materials which are themselves nanocomposites and which can be precursors for making at lower

temperatures, nanocomposite ceramics (or cermets) or single phase ceramics with a fine nanostructure, as shown below.



Most of the results presented here deal with the (B) situation; and the novelty of what is reported herein is that the presence of positive effects of the second (seed) phase on the reaction temperatures prove the importance of epitaxial effects in purely solid state reactions.

2. EXPERIMENTAL

As described in our earlier papers on diphasic gels (28,29) we have developed two different methods for making such materials. These are adequately summarized in Fig. 2. Readers are referred to the above-noted papers for details.

For the vast majority of experiments reported herein we have used Method II. We thoroughly mix two pre-existing sols at low viscosities so that we can

assume 'perfect mixing.' A gel is then formed from the mixed sol, dried and in part heated to an anhydrous (xerogel) condition, and used for further characterization and other reaction studies.

A great deal of our data on the thermodynamics of the xerogel→ceramics transformation was obtained by DTA, using the Harrop (Model TA700) and Perkin-Elmer (Model DTA1700) instruments. X-ray and SEM characterization has been done on most samples at various stages of the heating cycle. Optical microscopy proved to be significant in establishing the extraordinarily large corundum crystals obtained under certain conditions. Further details on the experimental conditions are included in the results.

3. RESULTS

3.1 Solid-State Epitaxial Effects in One-Component Diphasic Systems

3.1.1 The System TiO_2

A TiO_2 gel was made by the method described elsewhere (30). We have studied the solid phase in thin sol in detail by XRD and TEM and established that it is an anhydrous noncrystalline oxide, and that it shows no crystallinity until at least 200°C.

By adding a rutile-sol and mixing thoroughly prior to gelation of titania we created a series of diphasic gels so that the total solid phases contained 0.2, 0.5, ... 5% by weight of 0.1 μm rutile crystals. The unseeded and seeded gels were dried at 400°C to remove most of the organics prior to the DTA runs. Figure 3 presents the data. The DTA pattern shown at the top in Fig. 3 shows that the titania gel crystallizes to rutile (via an anatase stage) at approximately 900°C under the dynamic conditions of the DTA experiment. The most striking finding is that with 0.2% of rutile seeds, the diphasic xerogel transforms to rutile nearly 250°C lower than the unseeded TiO_2 xerogel, as is shown in the bottom curve of Fig. 3.

The DTA curves for higher concentrations of seeds show that there is

virtually no further effect after approximately 0.2%. It is obvious that seeding profoundly alters reaction and sintering of rutile ceramics.

3.1.2 The System Al_2O_3

3.1.2.1. DTA. In this case the experimental data have so far been obtained mainly for the slightly less straightforward case. We used a boehmite ($\text{AlO} \cdot \text{OH}$) sol (~20 nm particle), not precisely isoplethal with the sol of $\alpha\text{-Al}_2\text{O}_3$ seeds (~100 nm). However, the diphasic xerogel obtained at approximately 500°C when the boehmite has dehydrated to a ' $\gamma\text{-Al}_2\text{O}_3$ ' phase is truly isoplethal. The results comparing the unseeded and seeded gels with increasing wt. %'s of corundum seeds are shown in Fig. 4. These data are parallel to the TiO_2 data with a marked (~150°C) lowering of the $\theta\text{-}\alpha$ transformation exotherm from 1280° to 1150°C with the addition of only 0.1% seeds. Higher concentrations do not significantly lower the $\theta\text{-}\alpha$ monotropic transformation further.

3.1.2.2. Microstructure. In a completely separate series of experiments a similar boehmite sol was quickly gelled by evaporation and thin layers of the xerogel heated to 1150°C for 30 minutes. To our surprise we found that the $\alpha\text{-Al}_2\text{O}_3$ crystals which formed from what were originally 20 nm grains were 10–15 μm in diameter. Figure 5a shows them in polarized light. While detailed examination shows that there are low angle grain boundaries within the 10 μm grains, this is remarkable grain growth indeed. When the sol was seeded with the 0.2% $\alpha\text{-Al}_2\text{O}_3$ seeds and the experiment repeated, no large crystals could be found at all (Fig. 5b), the grain size was submicron and cannot be discerned optically. Details are reported elsewhere (31).

3.2 Epitaxial Effects in Two-Component Diphasic Systems

3.2.1 Addition to Alumina and 93% Al_2O_3 -7% MgO Gels

We have also explored the existence of hetero-homo and hetero-hetero epitaxy effects in diphasic xerogel-derived ceramics. This has been attempted

by the addition of crystalline seeds isostructural with $\alpha\text{-Al}_2\text{O}_3$ (i.e., Fe_2O_3 [corundum] and Cr_2O_3 [corundum]) to boehmite sols, and subsequent gelling. In order to check whether the effects being found were, in fact, structural epitaxy and not colloidal phenomena of the Zsigmondy model of protection colloids, we added also SiO_2 [quartz] seeds, and MgAl_2O_4 seeds. The quartz (see Fig. 6) shows no effect on the θ - α transition, and while Fe_2O_3 does show a lowering of 30°C , the Cr_2O_3 shows hardly any. The lattice mismatch with Fe_2O_3 is 5.86% and with Cr_2O_3 is 4.56% for the C parameter.

The 93% Al_2O_3 -7% MgO composition was studied as an example of a binary system in which both $\alpha\text{-Al}_2\text{O}_3$ and spinel would crystallize at equilibrium at 1150°C . It is also of particular technological significance since the composition of the 3M Regal abrasive grains is near this composition. Due to the known topotactic relations between the corundum and spinel structures manifest in the exsolution of the former from the latter and because spinel, unlike corundum, can hardly be made into a noncrystalline solid, it was considered worthwhile to investigate whether the spinel structure seeds could nucleate the spinel or the corundum phase. The data are shown in Figs. 6 and 7. The effect appears to be slight and not too surprisingly so. Epitaxy would of course, only occur on the (111) plane of spinel, and in general the cubic close packed oxygen array of spinel is not an effective substrate for the hcp face-shared octahedra of corundum. Figure 7 compares the effect of spinel and corundum seeds on the θ - α transformation as a function of composition. About 0.2 weight percent of seeds is clearly a saturation level. This would appear to correspond to the growth of grains of approximately $2\text{ }\mu\text{m}$ in diameter on seeds $0.2\text{ }\mu\text{m}$ in diameter (assuming spherical morphologies).

3.3 Compositionally Diphasic Nanocomposites Derived from Diphasic Xerogels

This paper has focussed on the very important changes which can be achieved by making nanocomposite precursor ceramic powders where the two

phases are structurally different. However, we have earlier demonstrated that compositionally diphasic xerogels differ even more radically in the reaction rates and patterns. Hoffman, Roy and Komarneni (29) have provided the data at the mullite composition where the mullite formation exotherm at 980°C is completely eliminated. These diphasic xerogels have been shown to sinter much better than the single phase xerogels as measured by the densities (Table 1) attained under identical conditions. We believe that the exceptional results obtained by Prochaszka (32) on transparent mullite ceramics may be attributed to this probable use of diphasic gels.

4. CONCLUSIONS

We have presented here sufficient data to show that we have discovered a generalized process to make a new class of materials--nanocomposites. By utilizing the guidelines of structural epitaxy even 0.1% of such seeds can affect the reaction and obviously therefore the sintering behavior. [The temperature and microstructure differences in such sintering of the α -Al₂O₃ seeded boehmite have been reported recently by our colleagues Kumagai and Messing (33).] Our other data show that we can fully expect that the generalized principle of solid-state epitaxy will therefore likely become widely used in ceramic processing.

However, of at least equal significance are the compositionally heterogeneous nanocomposite precursor mixtures made by the diphasic xerogel route. By designing binary ceramic powders as heterogeneous nanocomposites it should be possible to achieve very substantial (200-300°C) lowering of reaction and sintering temperature.

ACKNOWLEDGEMENT

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Table 1. Sintering Behavior of Single and Diphasic Mullite Xerogels as Measured by Densities.

Starting Materials	Density at 1200°C	Density Relative to Mullite (%)
Single Phase - $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Si}(\text{OC}_2\text{H}_5)_4$	2.71	85.4
Diphasic - $\text{AlOOH} + \text{Si}(\text{OC}_2\text{H}_5)_4$	2.92	92.0
Diphasic - $\text{AlOOH} + \text{Ludox} (\text{SiO}_2)$	3.05	96.2

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- Fig. 7. Transformation temperature of θ to $\alpha\text{-Al}_2\text{O}_3$ as affected by the concentration of spinel and $\alpha\text{-Al}_2\text{O}_3$ seeds.

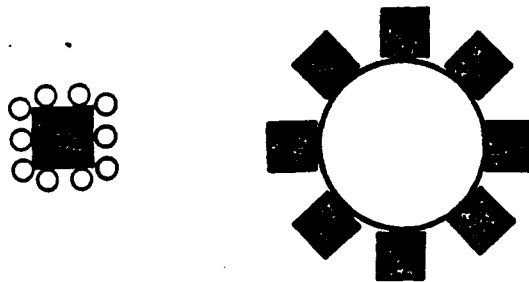


Fig. 1

MAKING NANOCOMPOSITES VIA DI-PHASIC XEROGELS

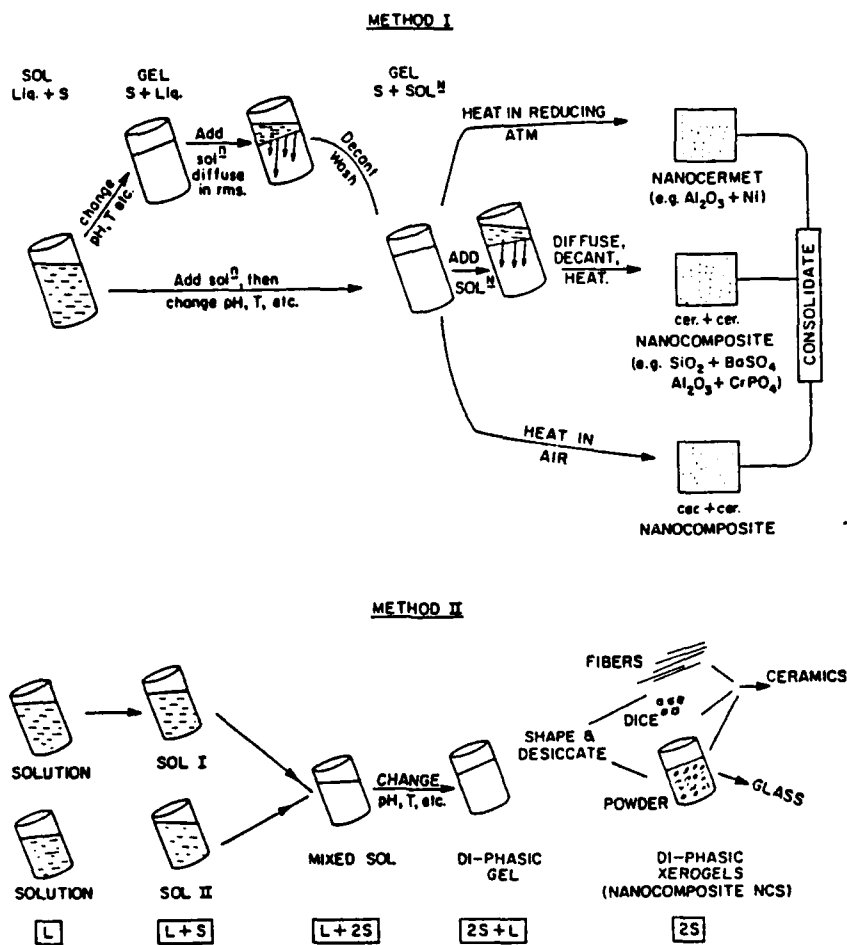


Fig. 2

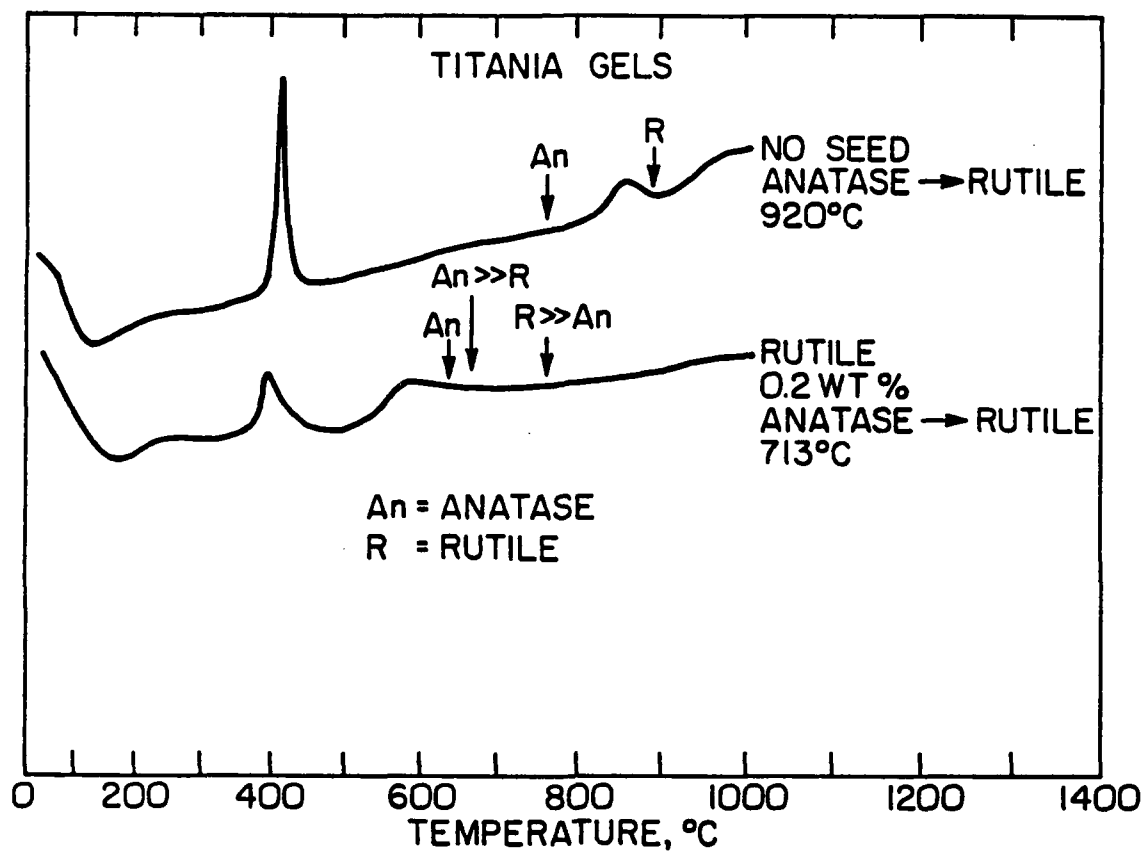


Fig. 3

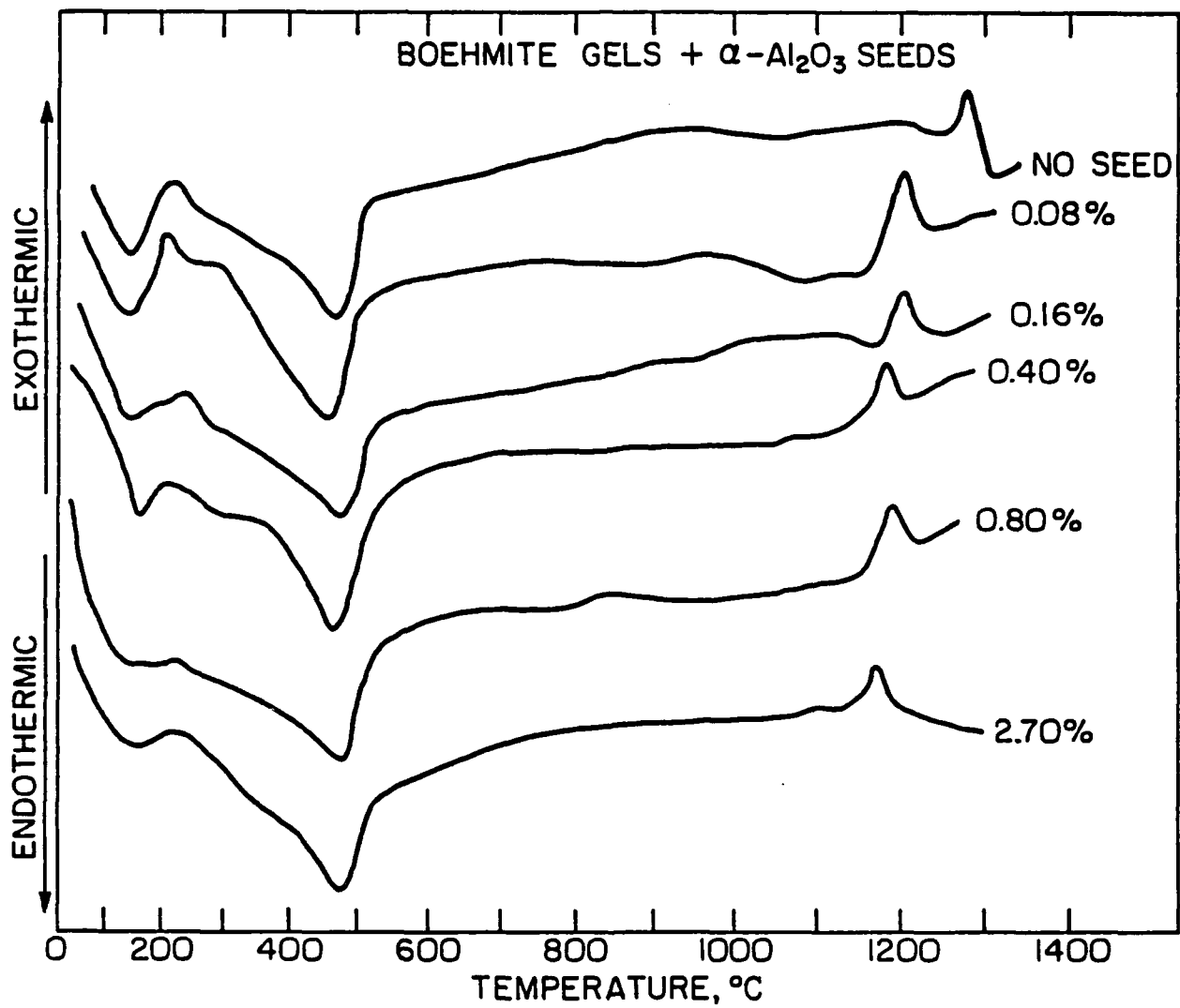


Fig. 4

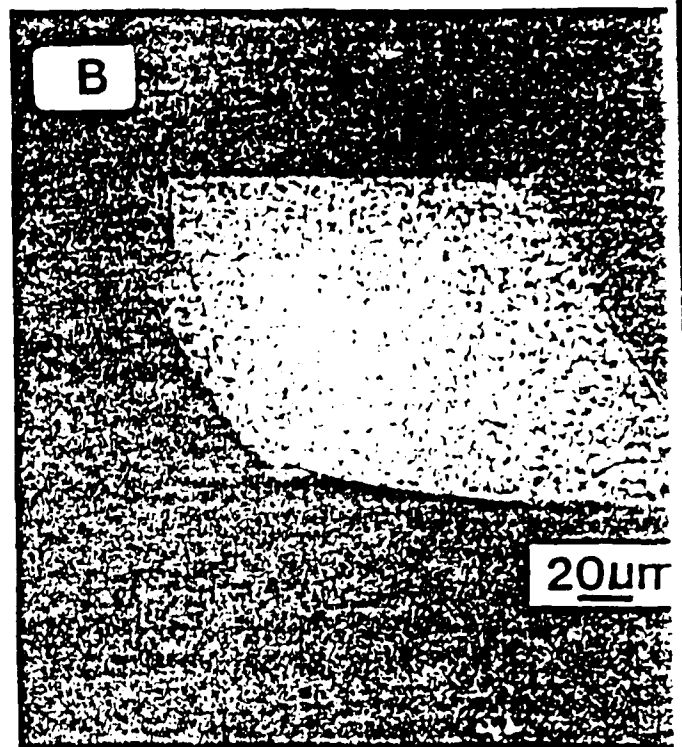
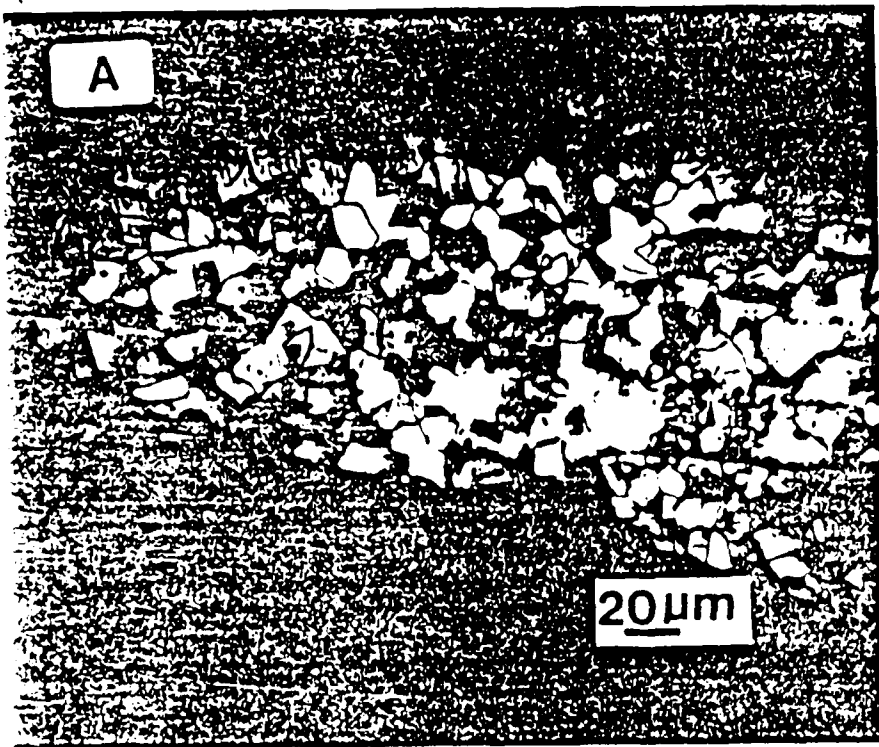


Fig. 5

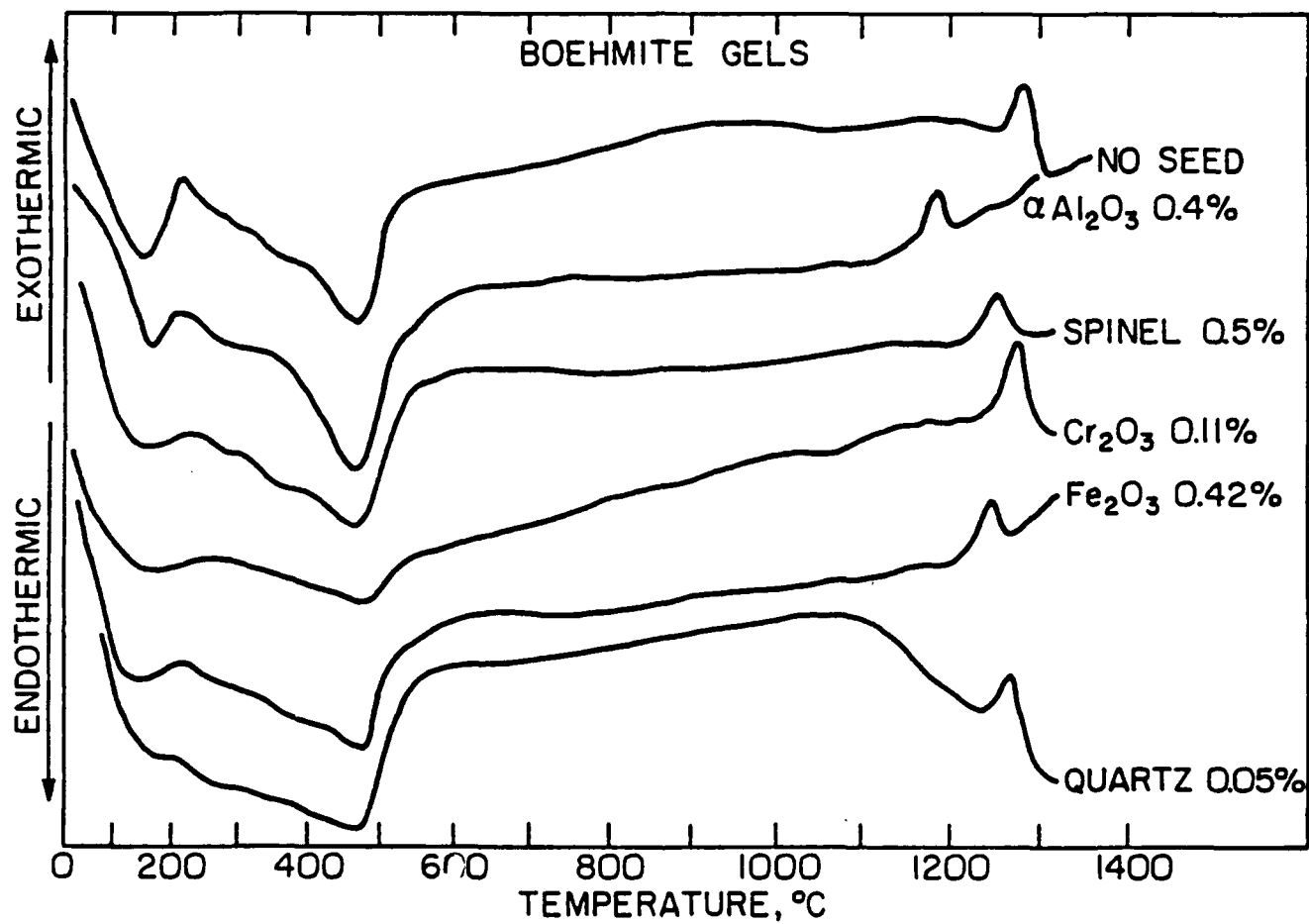


Fig. 6

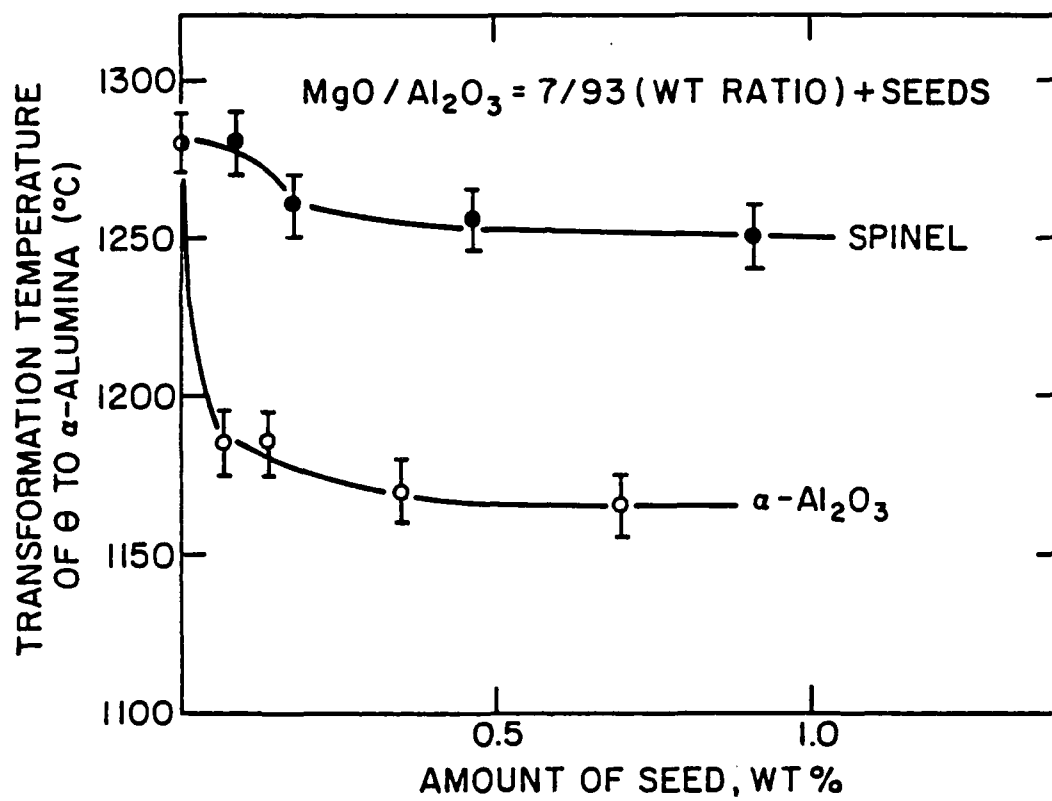


Fig. 7

Manuscript #1

Hydrothermal Route to Ultrafine Powders

Utilizing Single and Di-Phasic Gels

Hydrothermal Route to Ultrafine Powders
Utilizing Single and Di-Phasic Gels

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ABSTRACT

Hydrothermal preparation of ultrafine powders from gels in one-component and two-component oxide systems are reported here. Under specified conditions the process can yield almost monodisperse anatase (25-35 nm), rutile (100-300 nm), monoclinic zirconia (10-32 nm), tetragonal zirconia (~ 5 nm) and zircon (~75 nm). The control possible by use of diphasic gels is demonstrated by the fact that single phase zircon gel can be made into vermicular aggregates of zircon particles while the diphasic gel yields equant isolated particles. Ultra-fine corundum and mullite powders could not be made from the respective gels in the temperature range of 300° to 700°C, because of the extremely rapid kinetics. Large (10-50 μ m) beautifully faceted crystalline powders result instead. Fine (5 μ m) monodispersed corundum crystals, however, can be prepared from γ -Al₂O₃.

I. INTRODUCTION

Fine powder preparation is an integral part of the modern ceramic research and industrial processing and there are numerous methods of fine powder preparation. These have been reviewed by various authors (1-3). Among these, however, the hydrothermal method has largely been ignored. Yet from the preparation of single crystals of quartz for high technology applications to autoclaved cement block for low technology applications the hydrothermal route is now an established ceramic process in industry. With the ever increasing energy costs, the hydrothermal method could possibly become very attractive for fine powder preparation because of the low-temperatures involved in this method. This is one motivation behind this re-examination of the hydrothermal process for making fine ceramic powders.

Since 1948 we have developed and exploited hydrothermal processes for a variety of objectives at Penn State:

- Making highly crystalline ceramic powders at very low temperature (4-5).
- Synthesizing low temperature hydroxylated and anhydrous phases in hundreds of one to five component ceramic systems (6-9).
- Studying equilibrium in phase transitions which occur below about $\sim 1000^{\circ}\text{C}$ in oxide systems (10-12).
- Making highly ordered ceramic powders of phases which have the potential for site disorder, e.g. in feldspars for Al, Si (13), MgAl_2O_4 for Mg, Al (14) and $\text{Li Al}_5\text{O}_8$ for Li, Al (15).

These cases represent examples of special ceramic powders which can ONLY be synthesized by the hydrothermal process. No other method known can be used to make such powders. Moreover, just as only hydrothermal methods can give us more nearly site-ordered phases, so also only hydrothermal methods can give us reasonably perfect fine, crystalline powders. For example, it is impossible to obtain fine ($1\mu\text{m}$ or less) powders of crystalline quartz by grinding (16,17)

or by any other means.

In our early work some of the powders especially in the relatively complex composition of the (alkali) magnesia and/or alumino-silicates (7,8) such as the clays the powders were in fact very fine ($\ll 1\mu$). 1-2 μ m crystals such as in the $Mg_3Ge_2O_{10}(OH)_2$ (Magnesium-germanium chrysotile) (6) were regarded as large. However, it is only recently that Somiya and his co-workers have in a series of papers (18-21) utilized the hydrothermal method to make very fine (10-100nm) simple oxide powders of ZrO_2 , HfO_2 etc., of controlled composition and structure.

Likewise, very recent work has also focussed on 'reactive hydrothermal' synthesis of powders whenever the H_2O is a reactive component in the system. Here also Somiya and his co-workers have pioneered with their work on forming sintered or fine grained ZrO_2 and HfO_2 ceramics from Zr or Hf metal (22-24). Stambaugh and Miller (25) have utilized the activity change under hydrothermal conditions to precipitate oxide powders; and Kutty et al. (26) have cleverly reduced-metal hydroxides via this method.

In the present study we embark on examining the potential of the hydrothermal process in the preparation of fine ceramic powders in both one and two-component systems starting with single and di-phasic xerogels.

II. EXPERIMENTAL PROCEDURE

(1) Starting sol-gel materials

Titania gel was made²⁷ by initially mixing 18 ml of ethanol, 50 μ l of concentrated nitric acid and 720 μ l of water, followed by mixing with 4.8 ml titanium tetraethoxide, $Ti(OC_2H_5)_4$. The gelling occurred in 1-2 hours at room temperature. Titania gel was also made by the H_2O_2 treatment procedure.²⁸

Zirconia gel was made by initially mixing 18 ml of ethanol, 50 μ l of concentrated nitric acid and 720 μ l of water, followed by mixing with 13.6 ml of zirconium isopropoxide $\text{Zr-i-(OC}_3\text{H}_7)_4$. The gel was obtained immediately at room temperature. Other ZrO_2 gels which are almost clear were also made using higher concentrations of nitric acid. ZrO_2 precipitated by slow hydrolysis in air of Zr isopropoxide in propanol and zirconia precipitated from ZrOCl_2 in 1N NaOH were also used, the latter after washing free from soluble salts.

Alumina gel was made from boehmite, AlOOH (dispural) by dispersing in water and by dropwise addition of 1N HNO_3 while stirring. Translucent gel was obtained in about an hour. The gel was dried at 60°C prior to its use in hydrothermal experiments.

Single phase $\text{ZrO}_2\text{-SiO}_2$ (ZrSiO_4) gel was made by mixing appropriate volumes of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and tetraethoxysilane, $\text{Si(OC}_2\text{H}_5)_4$ and aging at 60°C . Clear gel was obtained in a few hours. Diphasic $\text{ZrO}_2\text{-SiO}_2$ gel was made by mixing appropriate volumes of zirconia sol and ludox, silica sol and aging at 60°C .

Single phase mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ gel was made by our standard methods (29) of mixing appropriate volumes of tetraethoxysilane and aluminum nitrate in alcohol-water solutions followed by aging at 60°C . This gel was denitrated at 400°C prior to the hydrothermal treatment. Diphasic mullite gel was made by mixing appropriate amounts of boehmite (dispural) with ludox followed by aging at 60°C and the sample was dried at 400°C .

(2) Hydrothermal treatment

The various gels along with water were loaded into gold capsules and sealed by cold-welding (30). In some cases HCl or HNO_3 was used as a mineralizer (see Table I). The sealed capsules were hydrothermally treated in cold-seal vessels at a range of temperatures and water pressures for different durations (see Tables I and II). The gold capsules were weighed before and

after hydrothermal treatment to check for the integrity of the capsules.

(3) Characterization of reaction products

After hydrothermal treatment under various conditions, the capsules were opened and the reaction products were separated and washed with deionized water. All the reaction products were characterized by powder x-ray diffraction (XRD) using Philips x-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. Some of the samples were characterized by scanning electron microscopy using an ISI-DS 130 instrument and by transmission electron microscopy (TEM) and selected area diffraction (SAD) using a 420 Philips microscope.

III. RESULTS AND DISCUSSION

(1) Ultrafine TiO_2 powders

The phases resulting from the hydrothermal treatment of titania gels are given in Table I. Titania gel made in H_2O_2 and treated at 450°C formed thin plates of anatase which are on the order of 25-35 nm (Fig. 1A). At 500°C , however, they formed very thin laths of rutile which are on the order of 200-350 nm (Fig. 1B). These thin lath-like rutile crystals could not be imaged at all in the SEM; the rutile mass appears to slide (Fig. 2). The reason for this unusual behavior is not clear but is associated with powder consisting of ultra-fine and thin particles. Titania gel made in ethanol crystallized to 20 nm anatase crystals (Fig. 1C) at 400°C and to 100-300 nm sized rutile plates (Fig. 1D) at 450°C . Titania gel made in ethanol transformed to rutile at a lower temperature than the titania gel made in H_2O_2 (Table I). Anatase can be crystallized from both gels at temperatures as low as 200°C . Thus hydrothermal treatment provides a method for making high surface area, ultrafine well crystallized anatase and rutile from titania gels at very low temperatures and modest pressures. The effect of pressure on the

crystallization of titania gels has not been investigated here but is not expected to be very significant and both the pressure and temperatures for obtaining these powders can no doubt be reduced if needed, especially if some 'mineralizer' is permitted.

(2) Formation of Ultrafine ZrO_2 powders

Somiya et al. have already prepared fine ZrO_2 powders (18,19). Our data on transformations of zirconia gels under different hydrothermal conditions are presented in Table I. All the hydrothermal treatments in this p-t range either resulted in baddeleyite (monoclinic ZrO_2) or baddeleyite + metastably persisting tetragonal ZrO_2 . Treatment of ZrO_2 gel in 0.1N HCl at 250°C resulted in 6-10 nm sized particles of monoclinic + tetragonal ZrO_2 along with some undifferentiated gel (arrows, see Fig. 3A). At 400°C, both monoclinic and tetragonal ZrO_2 remain in the presence of deionized water and 0.1N HCl but formed only monoclinic, ultrafine ZrO_2 in 1N HCl. At 450°C, only monoclinic ZrO_2 formed from zirconia gel and the particles are on the order of 10-30 nm in size (Fig. 3B). The particle size of the monoclinic ZrO_2 prepared here is smaller than that reported by Tani et al., (1981)⁷, but shows the same morphology. ZrO_2 precipitated in NaOH resulted in almost monodispersed rod-like monoclinic ZrO_2 (Fig. 3C) at 450 and 500°C. The particle size of the monoclinic ZrO_2 formed from zirconia gel is smaller than that made from ZrO_2 precipitate in NaOH. The presence of trace amounts of Na in the latter seemed to catalyze the reaction to form somewhat larger particles. Hydrothermal treatment at 500°C of zirconia obtained from slow hydrolysis of Zr-isopropoxide formed a mixture of ultrafine monoclinic and tetragonal ZrO_2 (Fig. 3D) powder. Pure tetragonal ZrO_2 was made at 120°C by treating amorphous ZrO_2 in 4N NaOH for 20 hrs. These results show that by appropriate adjustment of the hydrothermal conditions, ultrafine zirconia powders of the

desired crystal structure, including chemically pure and metastably persisting, can be obtained for potential use in modern ceramics, electronics, etc. Cubic ZrO_2 , was never observed.

(3) Formation of ultrafine well crystallized Al_2O_3 powders

Hydrothermal treatment of boehmite gel under a wide variety of different conditions never yielded ultra fine corundum powder (Table I) but formed large crystals (10-60 μm size) at 500°C (Fig. 4) after treatment for 24 hrs. Reduction in treatment time to 2 hrs at 500°C did not produce fine pure α - Al_2O_3 powders (Table I) but resulted in some corundum crystals + unreacted boehmite. Thus fine powders of α - Al_2O_3 could not be obtained from the boehmite gel. However, preparation of 5 μm corundum fine powder has been achieved by treatment of γ - Al_2O_3 at 450°C in 6 hrs.

(4) Hydrothermal treatment of single and diphasic mullite gels

Fine mullite powder could not be made from both single and diphasic mullite compositions under various hydrothermal conditions (Table II). Under the conditions used, the most stable phase appears to be hydralsite (8) as indicated by its presence in all the runs. Only in the case of diphasic mullite gel, some mullite could be detected by XRD. The crystallization of mullite in the diphasic gel unlike in the single phase gel may be attributed to the slow reaction in the former to form hydralsite because of discrete silica and alumina phases. Transmission electron microscopy revealed the presence of mullite needles of about 5 μm length (Fig. 5A) and SAD confirmed their presence (Fig. 5B). Rapid initial heating and heating to higher temperatures may be necessary to prevent the formation of hydralsite prior to the crystallization of mullite. These observations are consistent with the results recently reported by Somiya and coworkers (31).

(5) Hydrothermal treatment of single and diphasic zircon gels

There is a clear difference between the single and diphasic zircon gel reactions under hydrothermal conditions. The single phase zircon gel resulted in zircon only under all the treatment conditions whereas the diphasic gel resulted in zircon and monoclinic ZrO_2 at low temperatures and zircon only at high temperatures (Table II). Thus in the diphasic zircon gel, the ZrO_2 and SiO_2 sol particles appear to react independently where as in the single phase zircon gel the atomic scale mixing led to zircon formation under all conditions. The zircon formed from single phase gel aggregated into vermicular morphological entities (Fig. 6A) and shows crystals on the order of $\sim 75\text{nm}$ (Fig. 6B) whereas the zircon formed from diphasic gel shows thin platelets of $\sim 75\text{nm}$. Fine powders of zircon are, thus, prepared at a much lower temperature under hydrothermal conditions than possible under dry firing conditions.

IV. Conclusions

Ultrafine powders of titania, zirconia and zircon were prepared under hydrothermal conditions. The smallest particle size obtained in these studies for anatase ranged between 25 to 35nm, for rutile between 100 to 300nm for tetragonal zirconia between 5-6 nm and for monoclinic zirconia between 10-30nm. Zircon powders consisting of $< 75\text{nm}$ particles were obtained for both single and diphasic zircon gels. Hydrothermal processing of fine powders needs much lower temperatures than dry firing conditions and therefore, considerable energy savings are possible.

Acknowledgement

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TABLE I. XRD and TEM Analysis of Titania, Zirconia and Alumina Gels After Hydrothermal Treatment*

Sample	Hydrothermal Treatment	Reaction Products by XRD	Morphology by TEM
TiO ₂ gel-H ₂ O ₂	450°C/100MPa/3 hrs	Anatase	Thin plates (25-35nm)
TiO ₂ gel-H ₂ O ₂	500°C/100MPa/24 hrs	Rutile	Thin laths (200-350nm)
TiO ₂ gel-C ₂ H ₅ OH	350°C/100MPa/3hrs	Anatase	Thin plates (40-60nm)
TiO ₂ gel-C ₂ H ₅ OH	400°C/100MPa/3 hrs	Anatase	--
TiO ₂ gel-C ₂ H ₅ OH	450°C/100MPa/3 hrs	Rutile	Plates (100-300nm)
TiO ₂ gel-C ₂ H ₅ OH	500°C/100MPa/3 hrs	Rutile	Plates (300-1000nm)
ZrO ₂ gel-C ₂ H ₅ OH + 0.1N HNO ₃	250°C/4MPa/5 hrs	Very poorly crystalline Baddeleyite + tetragonal ZrO ₂	Plates (6-10nm)
ZrO ₂ gel-C ₂ H ₅ OH + 1N HCl	350°C/100MPa/3 hrs	Amorphous	--
ZrO ₂ gel-C ₂ H ₅ OH + 1N HCl	400°C/100MPa/3 hrs	Baddeleyite	Plates (20-40nm)
ZrO ₂ gel-C ₂ H ₅ OH + 0.1N HCl	400°C/100MPa/3 hrs	Baddeleyite + tetragonal ZrO ₂	--
ZrO ₂ gel-C ₂ H ₅ OH	400°C/100MPa/3 hrs	Baddeleyite + tetragonal ZrO ₂	--
ZrO ₂ gel-C ₂ H ₅ OH	450°C/100MPa/3 hrs	Baddeleyite	Plates (10-30nm)
ZrO ₂ gel-C ₃ H ₇ OH	500°C/100MPa/24 hrs	Baddeleyite + Tetragonal ZrO ₂	Plates (20-60nm)
ZrO ₂ -NaOH	450°C/100MPa/3 hrs	Baddeleyite	Rods (100-200nm)
ZrO ₂ -NaOH	500°C/100MPa/24 hrs	Baddeleyite	Rods (50-150nm)
AlOOH gel	300°C/50MPa/2hrs	Boehmite	--
AlOOH gel + 1.0N HCl	350°C/100MPa/3 hrs	Boehmite	--
AlOOH gel + 1.0N HCl	400°C/100MPa/3 hrs	Boehmite	--
AlOOH gel	400°C/100MPa/3 hrs	Boehmite	--
AlOOH gel + 1.0N HCl	450°C/100MPa/3 hrs	Boehmite	--
AlOOH gel	450°C/100MPa/3 hrs	Boehmite	--
AlOOH gel	500°C/100MPa/2 hrs	Boehmite, corundum	--
AlOOH gel	500°C/100MPa/3 hrs	Corundum, trace tohdite	--
AlOOH gel	500°C/100MPa/6 hrs	Corundum, trace tohdite	~20µm crystals
AlOOH gel	500°C/100MPa/24 hrs	Corundum	Twinned spindles (10-60µm)
AlOOH gel	550°C/100MPa/15 min	Corundum, akdalaitite, tohdite	--
AlOOH gel	550°C/100MPa/4 hrs	Corundum, tohdite?	--
AlOOH gel	600°C/100MPa/1 hr	Corundum	5-20µm crystals
AlOOH gel	700°C/70MPa/3 min	Tohdite, trace corundum	--
AlOOH gel	700°C/70MPa/15 min	Corundum + trace unidentified phase	--

*Treated with deionized water unless otherwise indicated.

TABLE II. XRD and TEM Analyses of Single and Diphasic Mullite and Zircon Gels After Hydrothermal Treatment with Deionized Water

Sample	Hydrothermal Treatment	Reaction Products by XRD	Morphology by TEM
<u>Mullite, $\text{Al}_2\text{Si}_2\text{O}_7$</u>			
Single phase gel	300°C/100MPa/12 hrs	Amorphous	--
Single phase gel	500°C/100MPa/12 hrs	Hydralsite	--
Single phase gel	600°C/100MPa/12 hrs	Hydralsite	--
Single phase gel	700°C/69MPa/4 hrs	Hydralsite	--
Diphasic gel	300°C/100MPa/12 hrs	Amorphous	--
Diphasic gel	500°C/100MPa/12 hrs	Hydralsite + unidentified phase	--
Diphasic gel	600°C/100MPa/12 hrs	Hydralsite + unidentified phase	--
Diphasic gel	700°C/69MPa/4 hrs	Hydralsite + mullite	Mullite needles (~ μm)
<u>Zircon, ZrSiO_4</u>			
Single phase gel	450°C/100MPa/4 hrs	Zircon	--
Single phase gel	500°C/100MPa/12 hrs	Zircon	--
Single phase gel	600°C/100MPa/12 hrs	Zircon	Vermicular aggregates (~75nm crystals)
Diphasic gel	450°C/100MPa/4 hrs	Zircon + Baddeleyite	--
Diphasic gel	500°C/100MPa/12 hrs	Zircon + Baddeleyite	Platy crystals (~75nm)
Diphasic gel	600°C/100MPa/12 hrs	Zircon	--

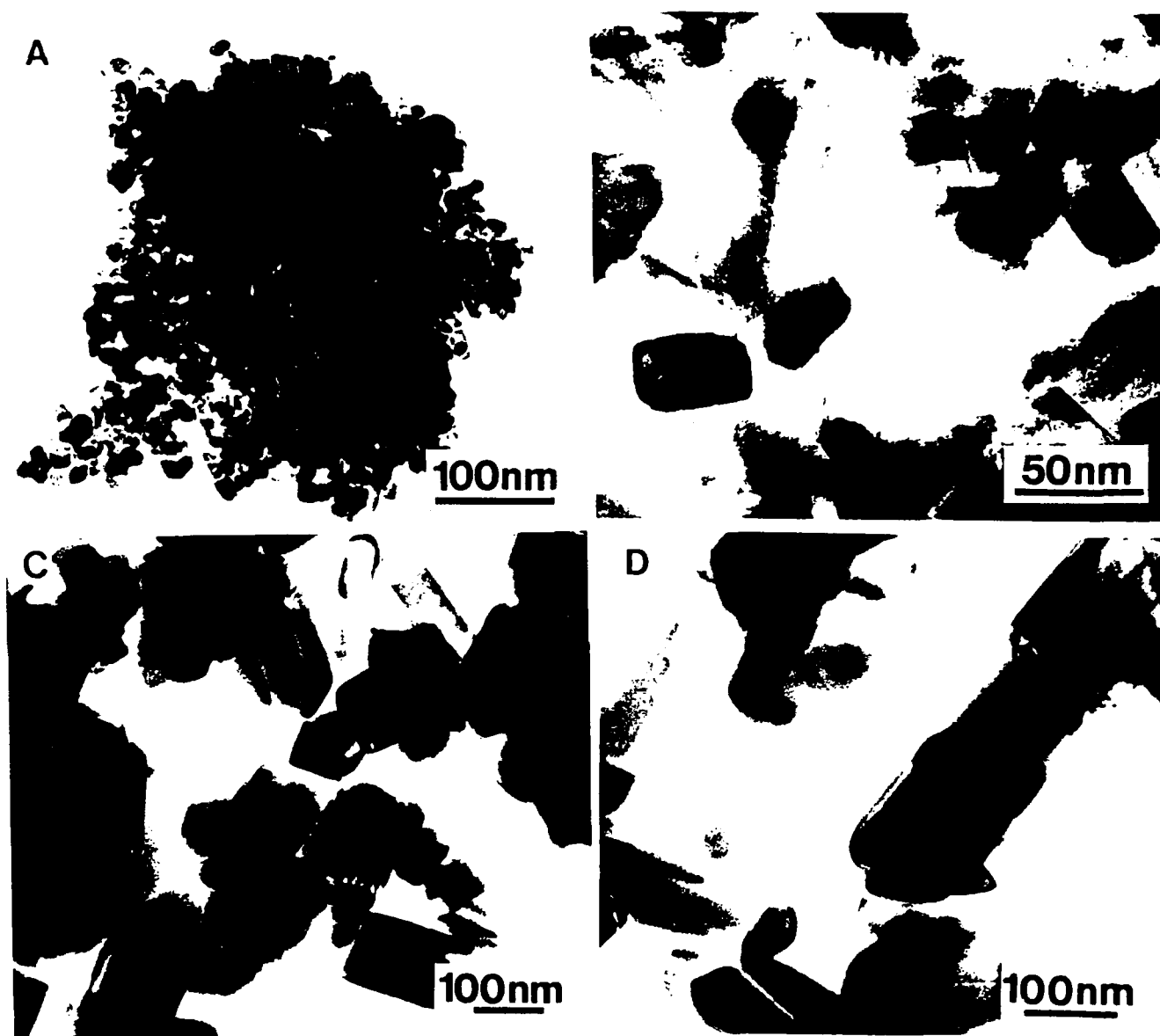


Fig. 1. Transmission electron micrographs of TiO_2 powders by hydrothermal treatment: (A) Anatase produced from TiO_2 gel in H_2O_2 at 450°C for 3 hrs. (B) Anatase produced from TiO_2 gel in ethanol at 350° for 3 hrs. (C) Rutile from TiO_2 gel in H_2O_2 at 500°C for 24 hrs. (D) Rutile from TiO_2 gel in ethanol at 450°C for 3 hrs. Pressure = 100 MPa in all cases.

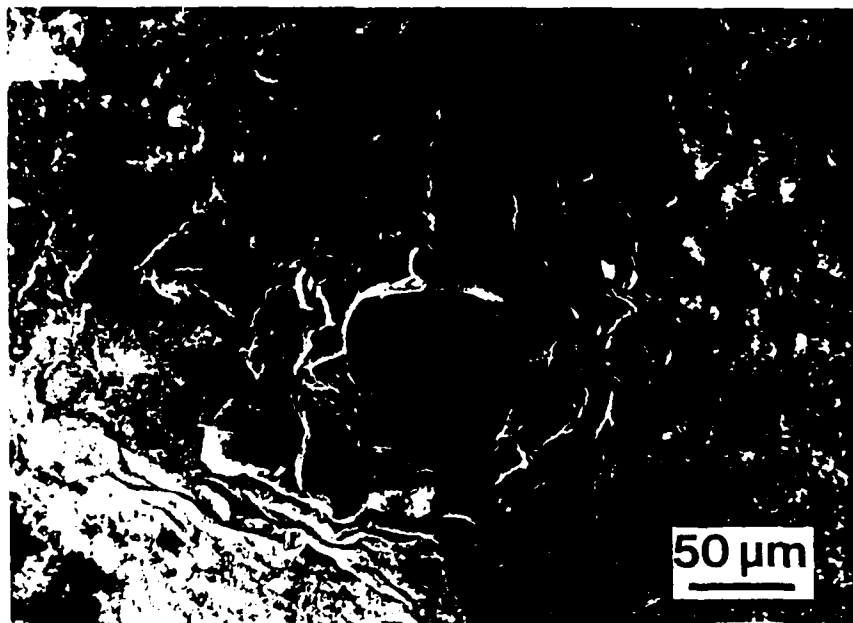


Fig. 2. Scanning electron micrograph of ultrafine rutile (same as Fig. 1C) showing the unexplained sliding behavior.

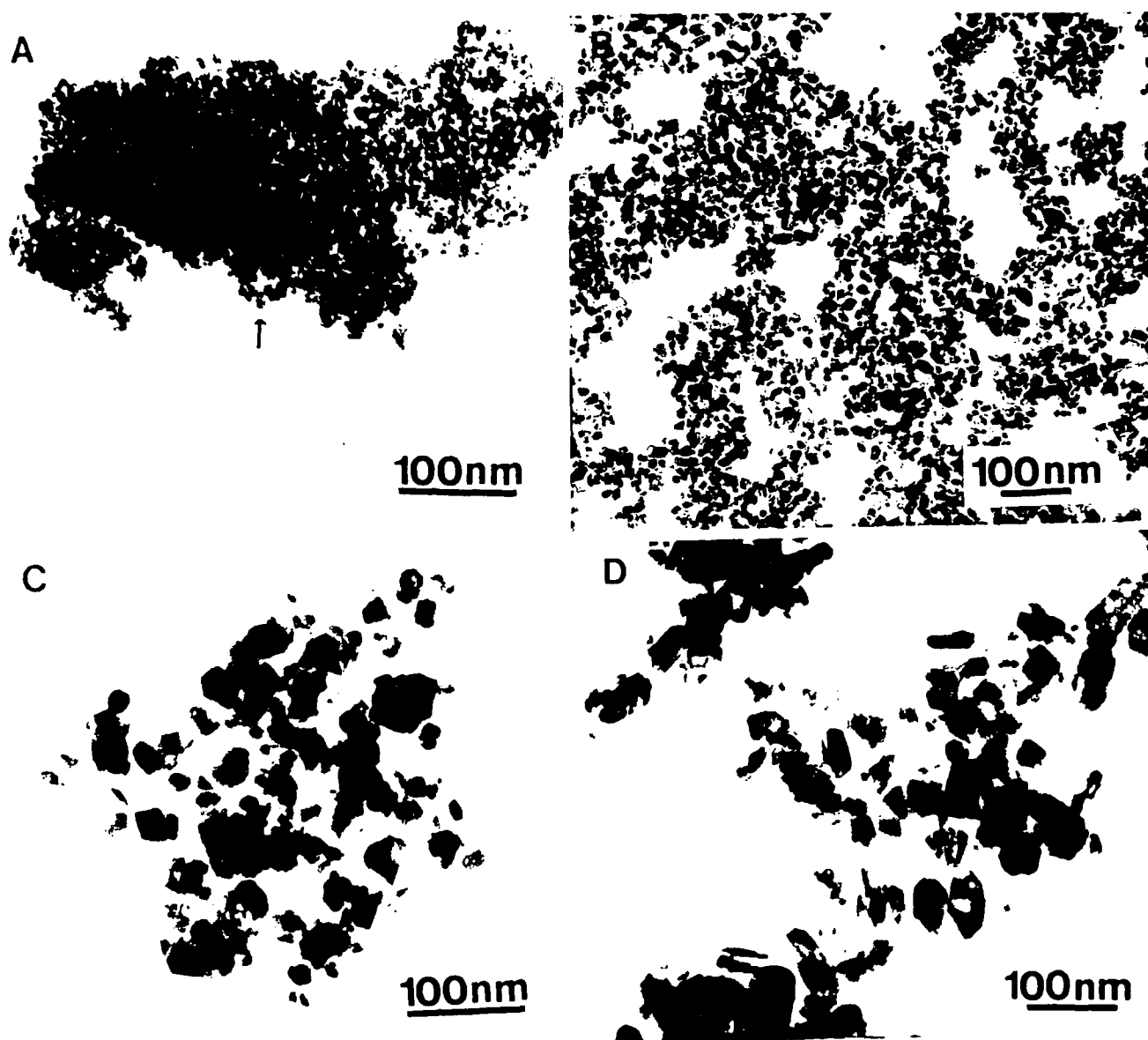


Fig. 3. Transmission electron micrographs of ZrO₂ powders by hydrothermal treatment: (A) Very poorly crystalline monoclinic and tetragonal ZrO₂ along with amorphous ZrO₂ (arrow) from ZrO₂ gel at 250°C/4MPa/5 hrs. (B) Monoclinic ZrO₂ at 450°C/100MPa/3 hrs. (C) Monoclinic and tetragonal ZrO₂ powder from ZrO₂ gel (slow hydrolysis in air) at 500°C/100MPa/24 hrs. (D) Monoclinic ZrO₂ from ZrO₂ precipitate (in NaOH) at 500°C/100MPa/24 hrs.

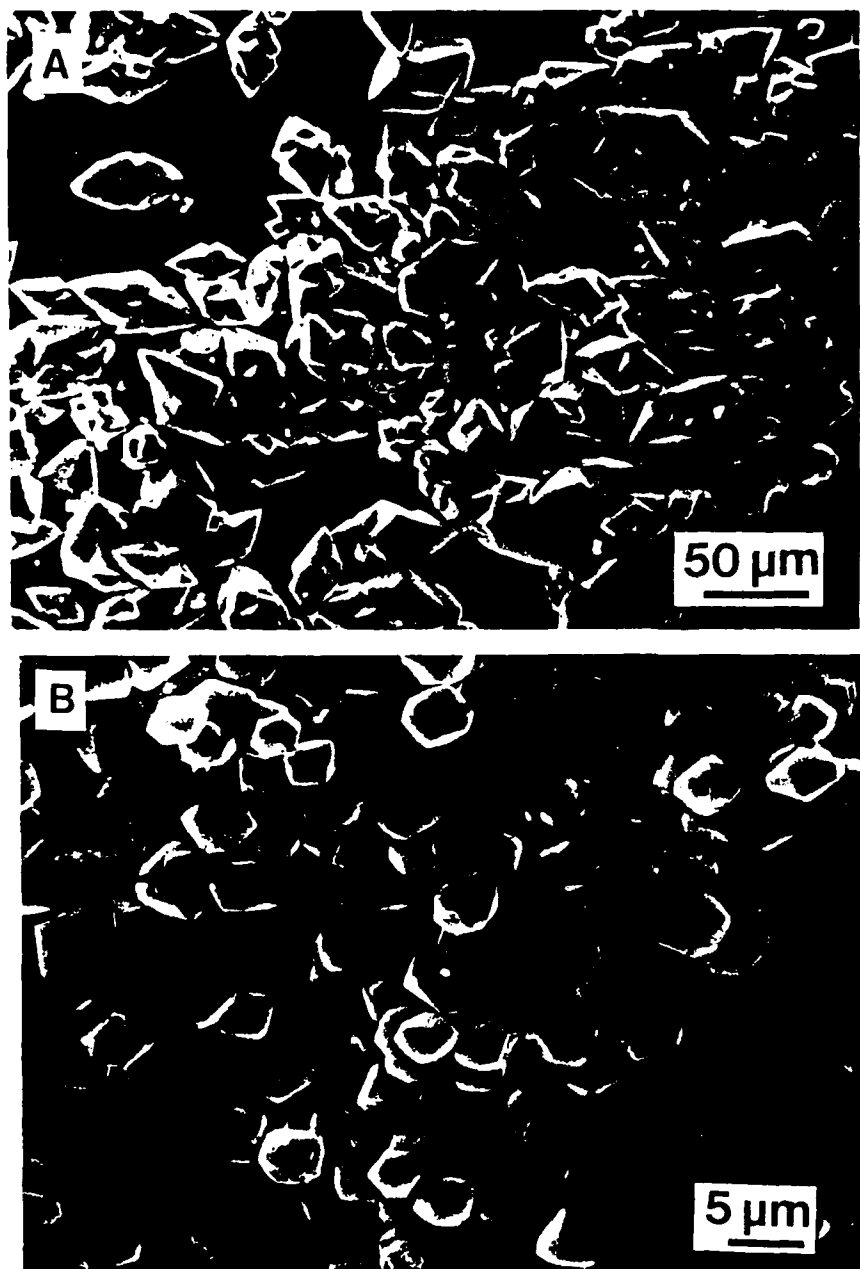


Fig 4. Large twinned corundum crystals made from boehmite gel at 500°C/100MPa/24 hrs (a) and small (~5 μm) corundum crystals made from $\gamma\text{-Al}_2\text{O}_3$ at 450°C/100 MPa/6 hrs (B).

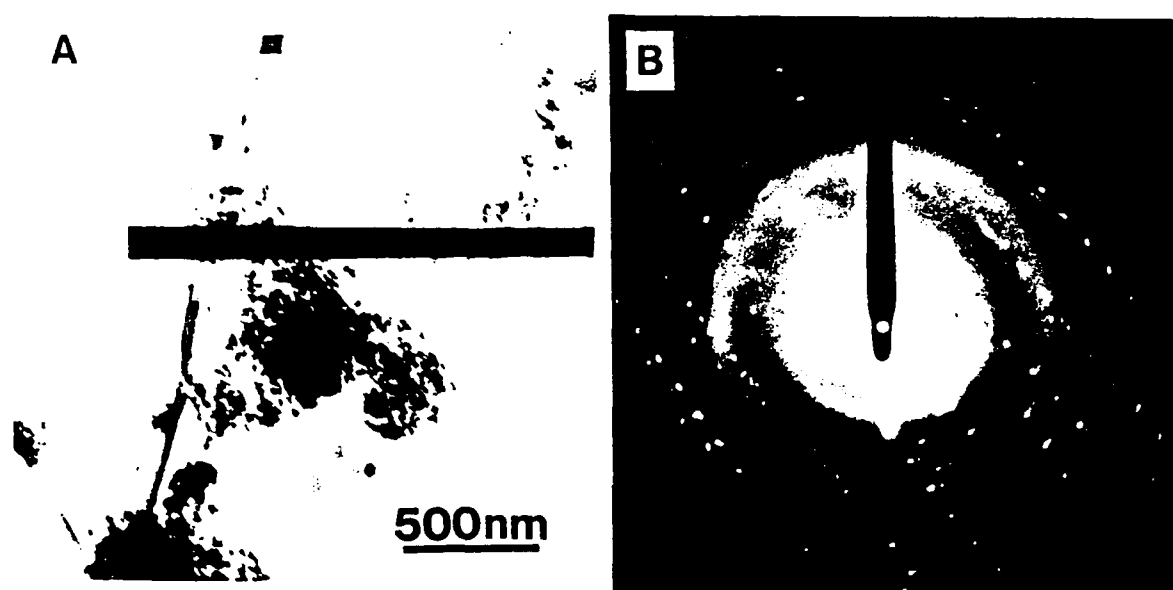


Fig. 5. TEM (A) and SAD (B) of mullite needles prepared from diphasic mullite gel at 700°C/69MPa/4 hrs.

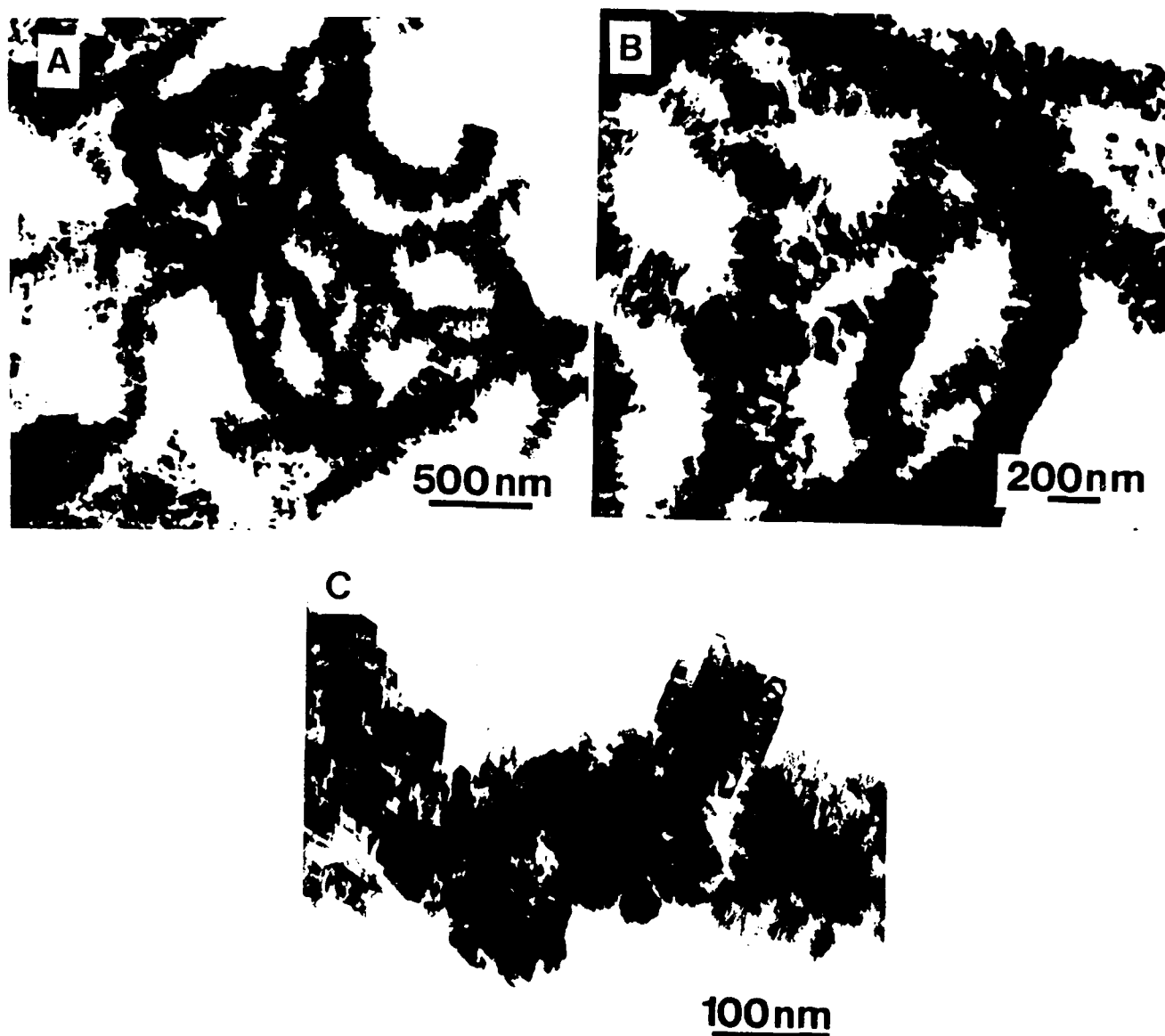


Fig. 6. Transmission electron micrographs of zircon gels after hydrothermal treatment at 500°C/100MPa/12 hrs: (A) Vermicular form of ZrSiO_4 made from single phase gel. (B) Same as A but at a higher magnification showing ~75nm crystals. (C) Platy ZrSiO_4 particles made from diphasic gel.

Manuscript #2

Natural Gel-Derived Ceramics:

Chemistry and Microstructure of Opal, Chert, Agate, etc.

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**NATURAL GEL-DERIVED CERAMICS: CHEMISTRY AND MICROSTRUCTURE
OF OPAL, CHERT, AGATE, ETC.**

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Introduction

The purpose of this work was to study the microstructure and mechanical properties of a group of naturally occurring silicates that are believed to form via a sol-gel or solution chemistry process below 100°C in order to learn how nature produces such hard and tough materials at low temperatures and then imitate the process in the laboratory. Moreover, during the course of the work a set of data was generated for these natural materials that can be used as a reference base for the next step of this work which is to discover treatment methods to enhance the hardness and toughness of these materials.

Experimental

Scanning Electron Microscopy

An ISI DS130 scope with a W filament was employed for microstructural and chemical determinations. The upper stage was used for microstructure determinations using flat, polished, and etched samples. Small chips were fractured from the edge of the sample so that both a polished and fracture surface was available for viewing on the same sample. These samples were etched in 10% HF for 15-60 seconds, depending on the material, and were Au-coated. The bottom stage was used for chemical analysis and the samples were flat, polished, unetched, and C-coated. An attached ux 7000 system collected and analyzed the x-rays emitted from the sample according to energy so elemental identification could be made.

Power X-Ray Diffraction

A Philips Norelco diffractometer with Ni-filtered Cu-radiation was used to determine the crystalline phase present and crystallinity of the quartz containing samples. Samples were powdered and packed into a glass cavity holder for examination. The crystallinity index was determined as described

by Murato and Norman (1976) using the ratio of the 212 and the neighboring peak in the quintuplet found at $68^{\circ}2\theta$. The index ranges from 1 to 10 where 10 is the best crystalline.

Materials

Samples were selected from five types of naturally occurring low-temperature-forming varieties of SiO_2 . The materials were obtained in bulk when possible, but many samples were only available in lesser quantities. The locality, quantity available (B=bulk, L=limited), and a description is given below for each group.

Opals

Three types of opals were selected for study. Two were naturally occurring varieties of Opal-A and Opal-CT and the other was Gilson synthetic opal. Only one sample of Opal-A was available in quantity. Table 1 gives details.

Jasper

Jaspers are fine-grained silicates that characteristically contain significant amounts of iron as an impurity as well as other impurities. They are typically shades of brown and dark reds (Dana, 1962). Table 2 contains information for the jaspers used in the study.

Agate

Agates are pure forms of fine-grained chalcedony (a fibrous variety of quartz) that commonly exhibit banding, pleasing coloration, and translucency. Table 3 gives information for the agates used.

Flint

Dana (1962) defines flint as a term used to describe siliceous nodules found in chalk and limestone. Flint is fine-grained and it typically shades of gray, brown, and black. Table 4 lists those flints used in the study.

Chert

Chert is very similar to flint but there is no sharp mineralogical distinction between them. However, cherts tend to be lighter in color than

Table 1. Selected Opal Types.

#	Sample	Quantity	Locality	Comments
1	Opal-A	B	Australia	white
2	Opal-A (1)	L	Andamooka, S. Aust.	white, some fire
3	Opal-A	L	Australia	white
4	Opal-CT (1)	L	Salt Creek, NSW	yellow-brown concretion
5	Opal-CT (1)	L	Lake Eyre, S. Aust.	porous, bulk wood replacement
6	Opal-CT (1)	L	Sunbury Victoria	yellow-brown
7	Opal-CT	L	Unknown	wood replacement retaining cellular structure
8	Gilson	L	Synthetic	milky white variety
9	Gilson	L	Synthetic	crystal white variety
10	Gilson	L	Synthetic	black variety

Table 2. Selected Jaspers.

#	Sample	Quantity	Locality	Comments
11	Bald Eagle	B	State College, PA	yellow
12	Bald Eagle	L	State College, PA	red
13	Omyhee	B		tan and light brown
14	Vera Cruz	B	Vera Cruz	dark brown
15	Green	B		dark green

Table 3. Selected Agates.

#	Sample	Quantity	Locality	Comments
16	Bloodstone	B		green with red spots
17	Brazil	B	Brazil	banded, light blues
18	Fire	B		poor fire
19	Montana	B	Montana	translucent, white
20	Moss	B		clear with green dendrites
21	Petrified Wood	B	Arizona	red, yellow, purple
22	Botswana	B		banded, dark
23	Blackskin	B		transparent

Table 4. Selected Flints.

#	Sample	Quantity	Locality	Comments
24	Black	B	Oak Hall, PA	black and uniform
25	England	B	England	gray, contains carbonate

Table 5. Cherts Selected for Study.

#	Sample	Quantity	Locality	Comments
26	Burlington	B	Burlington, IL	cream color
27	Oolitic	B	State College, PA	gray, well silicified
28	novaculite	B	Arkansas	white

flints (Dana, 1962). Table 5 lists the cherts studied. It should be noted that novaculite may be considered a slightly metamorphosed chert.

Results

X-Ray Diffraction

Table 6 lists the phases detected by x-ray diffraction on powdered samples and the crystallinity index obtained for quartz containing samples.

The opals are of two types as indicated by the nomenclature. One gives an amorphous hump at a d-spacing of $\sim 4\text{\AA}$ and the other a disordered cristobalite-tridymite pattern. Sample #7, an opalized wood, is the only natural opaline material containing a detectable quantity of quartz. The traces for the Gilson opals all have an amorphous hump at a d-spacing of $\sim 4\text{\AA}$ and also shows a cubic zirconia pattern.

The jaspers are the most impure of all the silicates studied and may contain hematite, goethite, or feldspar as minor impurities. Only the Vera Cruz jasper contains no detectable crystalline impurities. The agates, flints, and cherts are quartz except for the flint from England which contains a minor amount of calcite.

The quartz found in the samples is mainly poorly to moderately crystallized with only 4 samples of 19 having an index of 5 or greater.

Scanning Electron Microscopy

The average size range for the fundamental observable microstructural units, as well as the maximum observed flow size, and the chemistry and elemental distribution of the samples are given in Table 6 and Figures 1-6.

Generally, the basic microstructural unit observed for all samples examined was a ball (as seen in Figures 1-5) of greater or lesser sphericity, depending on the particular sample. The size range of the balls for all samples was on the order of $0.1\text{--}0.5\mu$. Some samples exhibited a finer substructure of balls $0.01\text{--}0.05\mu$ in diameter. Figure 1 is the best example of the observed fine structure. There is a question as to the cause of the fine structure seen in the samples. It is possible that it is an artifact of the Au-coating process and not a true fine structure of the samples.

Also listed in Table 6 is the maximum observable flow size. The number given is the approximate diameter of the largest observed flow size since most of the samples had roughly spherical flaws that could be considered as

Table 6. X-Ray and SEM Results.

#	Sample	XRD Phases	Crystal- linity Index (1-10)	XES Chemistry	Elemental Distribution	Micro- Structure (μ)	Maximum Flaw Size (μ)
1	Opal-A	A		Si(Al,Ca*)	HD	0.2-0.3f	0.4
2	Opal-A	A		Si(Al,K,Ca, Fe*)	HD	0.1-0.2f	1
3	Opal-A	A		Si(Al,K,Ca Fe*)	HD	0.1-0.2f	0.5
4	Opal-CT	CT		Si(Al,Fe,Mg, K,Ca*)	HD	2-3f	7
5	Opal-CT	CT		Si(Al,Cl*)	HD	0.1-0.2	6
6	Opal-CT	CT		Si(Fe,Al)	Fe-IS	0.05-0.15	40
7	Opal-CT	CT,Q	2.0	Si(Al,Mg*)	HD	0.1-0.2	15
8	Gilson	A,Z		Si(Zr)	HD	0.1-0.2f	0.5
9	Gilson	A,Z		Si(Zr)	HD	0.1-0.2f	0.5
10	Gilson	A,Z		Si(Zr)	HD	0.1-0.2f	0.3
11	Bald Eagle Jasper	Q,H	1.7	Si(Fe)	Fe-IS	0.1-0.2	40
12	Bald Eagle Jasper	Q,H,G	1	Si(Fe)	HD	0.1-0.3	3
13	Owyhee Jasper	Q,F	4.8	Si(Al,K,Fe, Mn*)	K-RF Fe-IS Mn-IS	0.1-0.2f	15
14	Vera Cruz Jasper	Q	4.1	Si(Fe)	Fe-IS	0.05-0.15	10
15	Green Jasper	Q,F	7.0	Si(Al,K,Fe, Ca,Na*,Mg*)	K-RF Fe-IS	0.1-0.2f	15
16	Bloodstone Agate	Q	1.6	Si(Fe,K*)	Fe-IS	0.1-0.2f	10
17	Brazil Agate	Q	1	Si(Al*)	HD	0.1-0.2	0.2
18	Fire Agate	Q	1.4	Si(Fe,Ti)	Fe,Ti films	0.1-0.2	10
19	Montana Agate	Q	1.1	Si	--	0.05-0.15	1
20	Moss Agate	Q	1.4	Si(Fe,K,Cl)	Fe,K-D K,Cl xls	0.1-0.2	30
21	Petrified Wood	Q	4.6	Si(Fe,Al*,Mg*)	HD	0.1-0.5	1
22	Botswana Agate	Q	2.9	Si(Al*)	HD	0.1-0.3	1
23	Blackskin Agate	Q	1.1	Si(Al)	HD	0.1-0.4f	0.2
24	Black Flint	Q	8.4	Si(Al*)	HD	0.5-4f	5
25	Flint	Q,C	2.0	Si(Ca,K*,Cl*)	Ca-IS K,Cl xls	0.1-0.2	2
26	Chert	Q	2.7	Si(Al,Mg*)	HD	0.1-1	1
27	Oolitic Chert	Q	5.0	Si(Ca*)	Ca-IS	0.4-5	30
28	Novaculite	Q	7.7	Si(Al*)	HD	1-5	10

A = amorphous
 Q = quartz
 CT = cristobalite-tridymite
 Z = zirconia
 F = feldspar
 H = hematite
 G = goethite
 C = calcite

() = small quantity
 * = trace quantity
 HD = homogeneous distribution
 D = dendrites
 IS = irregular spheres
 RF = associated with relic feldspar grains
 xls = crystals
 f = fine structure $\sim 0.2\mu$

spheres.

The only samples that did not show a structure made of balls was the Arkansas novaculite and the Black flint from Oak Hall. Figure 6 clearly shows a structure of polyhedral grains instead of $0.1-0.5\mu$ balls. Figure 5 shows the beginning of polyhedral grain development from balls.

The major element in all samples as detected by x-ray energy spectroscopy was Si. Most samples contained only minor quantities of other elements, and many times only in trace amounts. The sample with the greatest impurity concentration, according to peak intensities, is the yellow Bald Eagle jasper (Figure 7).

Summary of Conclusions

1. All the materials examined appear to have been formed initially by the random aggregation of $1000-5000\text{\AA}$ balls by a sol-gel or solution chemistry process presumably below 100°C .

2. The synthetic opals are composed of balls $1000-2000\text{\AA}$ in diameter, much like the natural opal analogues.

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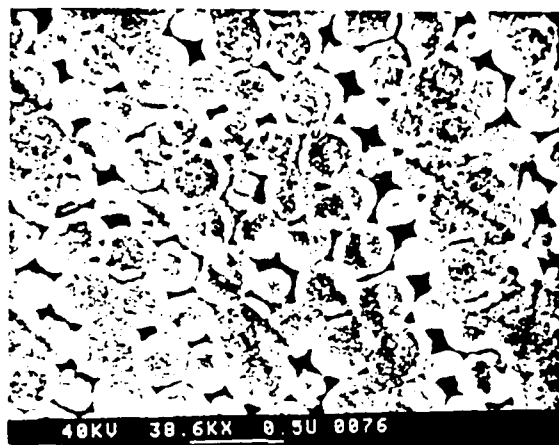


Fig. 1. Microstructure of White opal A, Australia.

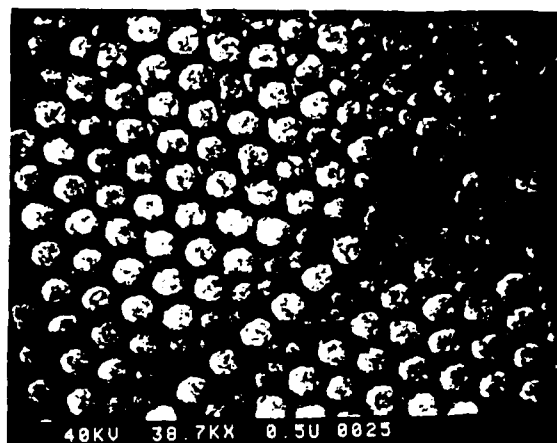


Fig. 2. Microstructure of synthetic opal, Gilson crystal white.

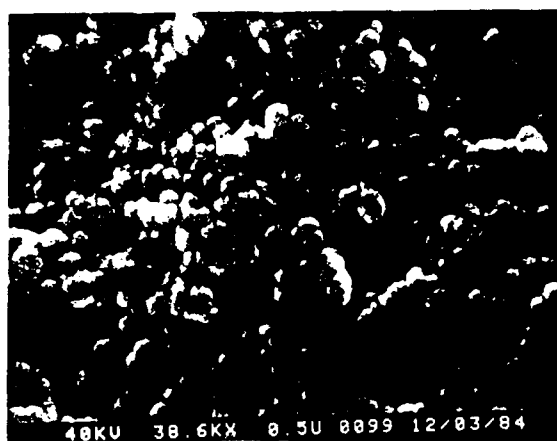


Fig. 3. Microstructure of agate, Montana.

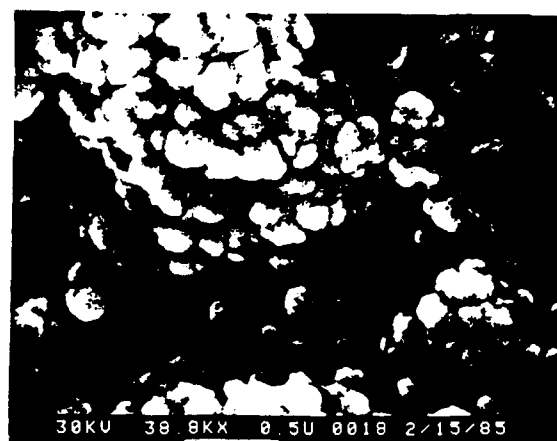


Fig. 4. Microstructure of jasper, Pennsylvania.

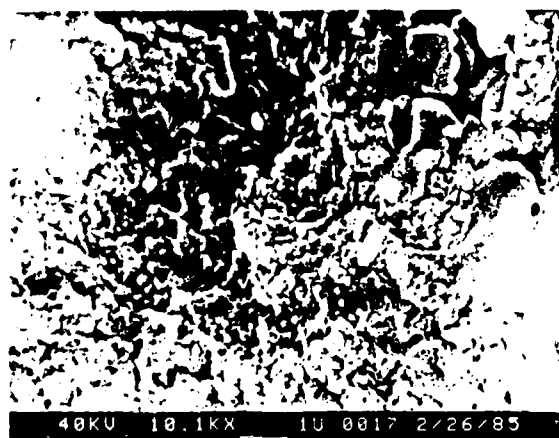


Fig. 5. Microstructure of Burlington chert.



Fig. 6. Microstructure of black flint.

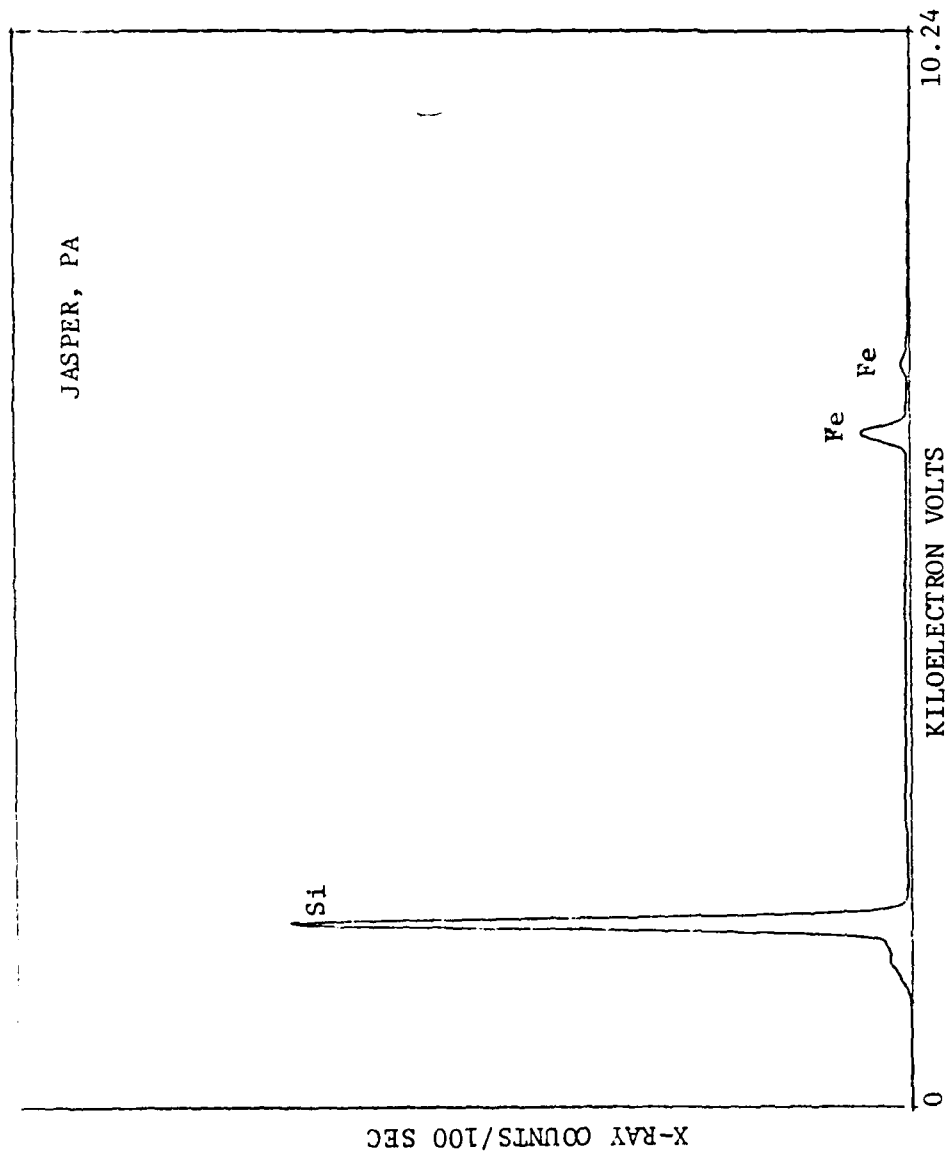


Fig. 7. EDX analysis of jasper, Pennsylvania

Manuscript #3

Colloidal Sol-Gel Processing of Titania-Silica Glasses

COLLOIDAL SOL-GEL PROCESSING OF TITANIA-SILICA GLASSES

BY

C. P. Scherer and C. G. Pantano

The best known ultra-low expansion glass is a 7% TiO_2 -93% SiO_2 composition which must be processed by chemical vapor deposition (CVD). Clearly, the fabrication of large pieces for space structures is difficult, time-consuming and expensive using the CVD process. This ultra-low expansion glass composition has also been successfully processed with a single-phase alkoxy sol/gel approach, but again, the preparation of large pieces is difficult due, in this case, to the excessive shrinkage encountered. We have been developing a diphasic sol/gel approach to this problem based upon the use of high-purity colloidal silica which is gelled in a titanium-doped solvent, or is co-gelled with a titania/silica alkoxy solution. The use of colloidal silica should reduce the cost, accelerate the gelation and drying, and minimize the drying and firing shrinkages.

After extensive evaluation of various raw materials and gel preparation methods, two colloidal sol-gel processes have been developed to produce 7-10 wt % titania-silica glasses for low-expansion substrates. The source of titanium in both processes is titanium isopropoxide, an extremely pure metal alkoxide (Alpha Products, Inc.). The colloidal silica powders (Degussa's Aerosil 200 m^2/g and Cabot's Cab-O-Sil 200 m^2/g and 400 m^2/g) are made by flame hydrolysis technique, and thus, are also extremely pure (>99% SiO_2). A variety of thermal and microstructural analyses have been used to characterize the processing and sintering of the gels, while the coefficient of thermal expansion has been the property of most interest.

The two processes that have been developed are similar. They involve mixing the 'stabilized' organometallic titanium-alkoxide (see below) with silica powder in a conventional blender to form a sol. The sol is then poured into glass tubes (13 mm diameter and 80 mm length) which are sealed and heated to 60-80°C to promote gellation. After a time, the gels are stiff enough to be removed from the tubes and dried. The dried gels have a density that is $\approx 25\%$ of the theoretical value. An initial heat treatment of the dried gels in oxygen to 350-500°C (15-20 hrs) is used for the removal of organic residuals. The pre-sintered gels are then fired at 1225-1250°C for complete densification. The final densities - typically 2.15 to 2.25 g/cm³ - are comparable to glasses of the same composition made by chemical vapor deposition (e.g. Corning's ultra-low expansion ULE-7971).

The titanium isopropoxide (TIP) is extremely reactive and readily hydrolyzes and precipitates in water. Therefore, the TIP must be 'stabilized' before it can be incorporated into the aqueous silica sol. The method of stabilization and incorporation of the TIP in the sol is the major difference between the two processes that have been developed.

Method A involves the drop-wise addition of a mixture of TIP, propanol, and acetyl acetone (AcAc) into a solution of tetraethylorthosilicate (TEOS), ethanol, water, and AcAc. The colloidal silica powder can then be added to this mixture to form a sol. The sol must be heated to 60-65°C for gelation to occur, and a very slow drying is required (≈ 30 days) in the sealed tubes to prevent cracking. Likewise, a very slow heating rate must be used during the initial presintering of these gels (i.e., 25°C/hr to 500°C). Finally, the gels can be heated at 100°C/hr in air to 1250°C.

The dried gels produced by Method B contain more organic residuals, but for the same reason the gellation and drying can be accelerated because the gels are less susceptible to cracking. This method comprises mixing the TIP

with ethylene glycol and citric acid. The mixture is heated to 115°C to evolve the propanol from the system. This mixture is now miscible and stable in water. Silica powder is then added to a 50-50 mixture of this titanium-glycol and water. A two-step heat treatment of the sol is needed. First, heat treating to 40°C allows for swelling and evolution of the bubbles in the sol while they are being cast (a vacuum treatment was attempted here, but was insufficient to remove the bubbles). Subsequent heating to 70-75°C promotes gellation. The stiff gels are then extracted from the tubes and dried overnight in air at room temperature. Again, an initial pre-sintering of the dried gels to 350°C in 10-15 hours allows for removal of organics as shown by the upper two differential thermal analyses (DTA) in Figure 1.

The densification of these gels begins at 1000°C; the densification behavior is studied by using a constant load head (50g wt) on the dilatometer. The gel attains full density at 1225°C. A variety of sintering atmospheres were evaluated (ambient, helium oxygen, and vacuum), but it was found that an air atmosphere yielded the best results.

Although Method B is clearly more convenient and thus is being further developed, it is noteworthy that both processes yielded fully dense glasses that could not be readily distinguished. The glasses are always translucent, and thus some attention has been focused upon the crystallization behavior. The DTA traces in Figure 1, especially the lower one for the pre-sintered glass, show no evidence for extensive crystallization of the matrix. Nevertheless, the x-ray diffraction patterns in Figure 2 reveal the development of sharp - albeit weak - crystalline peaks during the densification. Transmission electron microscopy (TEM), energy-dispersive x-ray analysis (EDS) and electron diffraction have verified the presence of titanium-rich microcrystallites

($\approx 150\text{\AA}$ dia.) that are uniformly distributed in silica-rich amorphous matrix. These can be seen quite clearly in Figure 3. It is significant, though, that heating of the glasses at 1225°C for 11 hours did not coarsen these crystals (which are believed to be anatase) or promote the crystallization of rutile.

The coefficients of thermal expansion (CTE) for the dense glasses were measured on a Theta differential dilatometer using a fused silica reference. The CTE of the glasses made via Method A were slightly higher than for those made by Method B. The CTE values for the glasses were in the range $2 - 3.4 \times 10^{-7}/^{\circ}\text{C}$. The softening point of the glass was about 1100°C .

It is worth mentioning finally that powders were made from the dried and presintered gels of Method B. These powders were pressed into pellets and then were vacuum hot pressed at 1400°C and 3,200 psi. These glasses were fully dense, amber in color and transparent. Nevertheless, they also contained microcrystallites of anatase, but had a CTE of $0.24 \times 10^{-7}/^{\circ}\text{C}$.

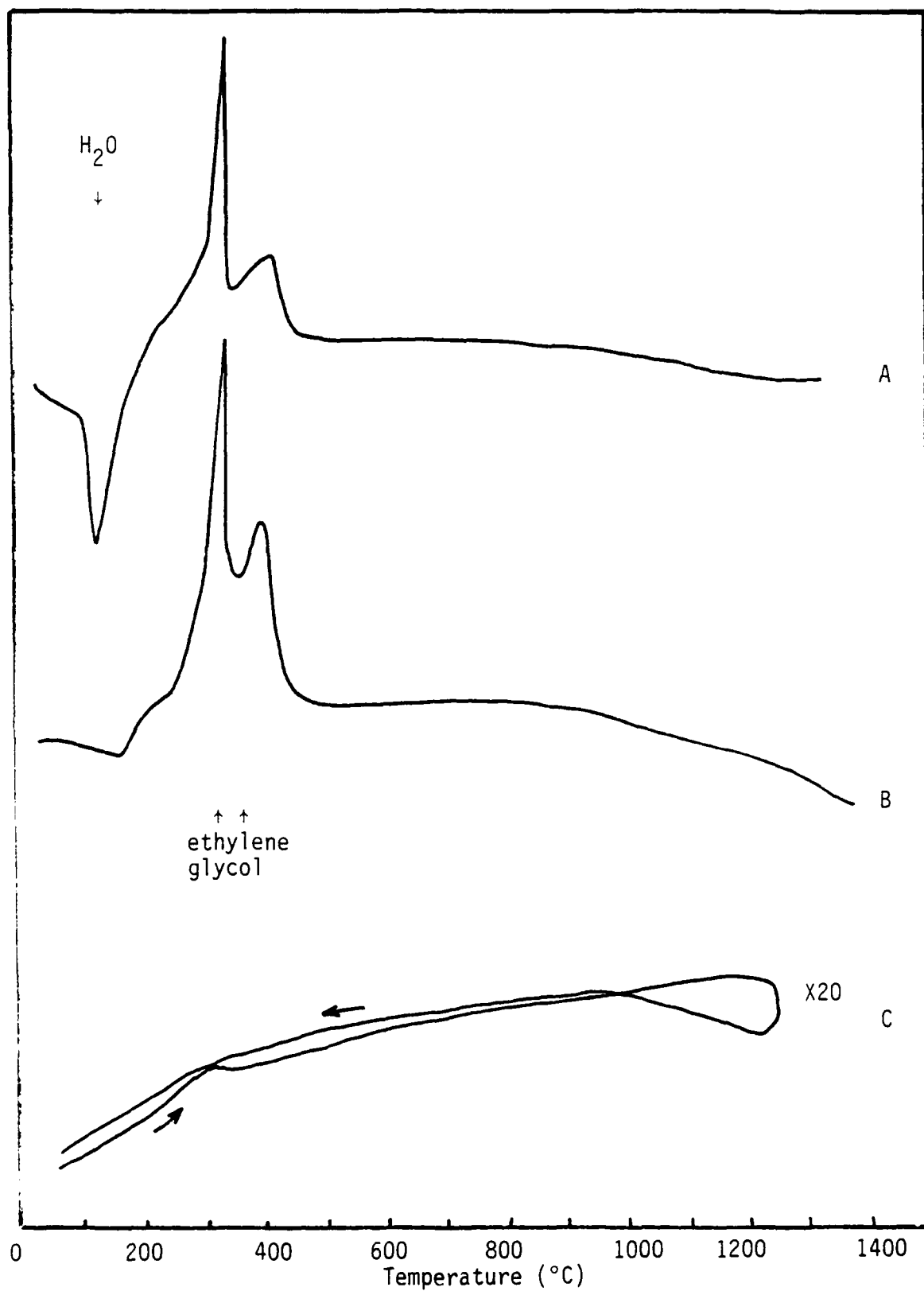


Figure 1. DTA analyses of gels made by Method B: (A) fresh sol; (B) gel dried at room temperature; (C) gel presintered to 400°C (for removal of organics).

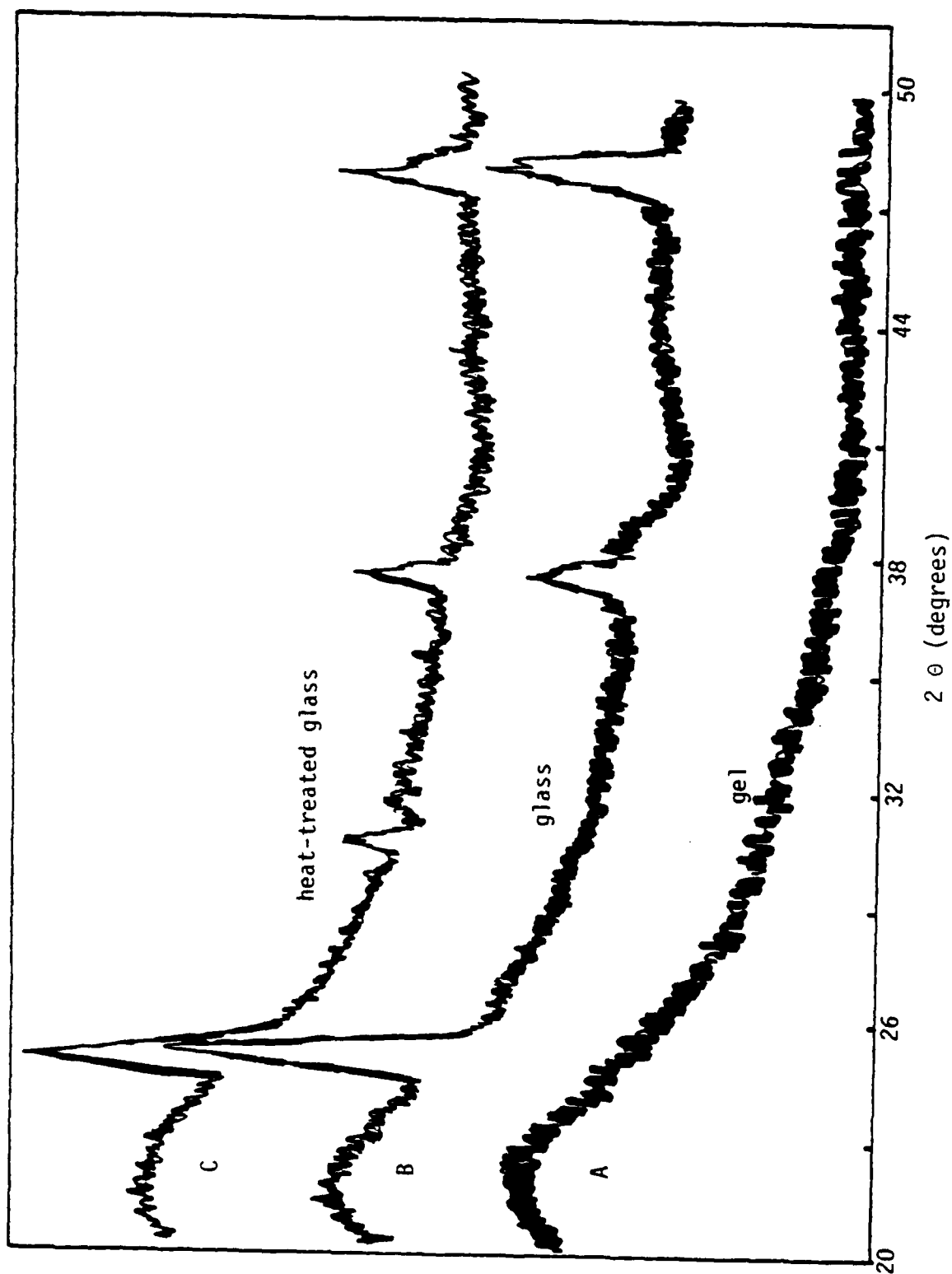


Figure 2. X-ray diffraction patterns of gels made by Method B: (A) gel presintered to 400°C to remove organics; (B) gel sintered to 1225°C for densification; (C) sintered and soaked at 1225°C for 11 hours; peaks are due to anatase phase.

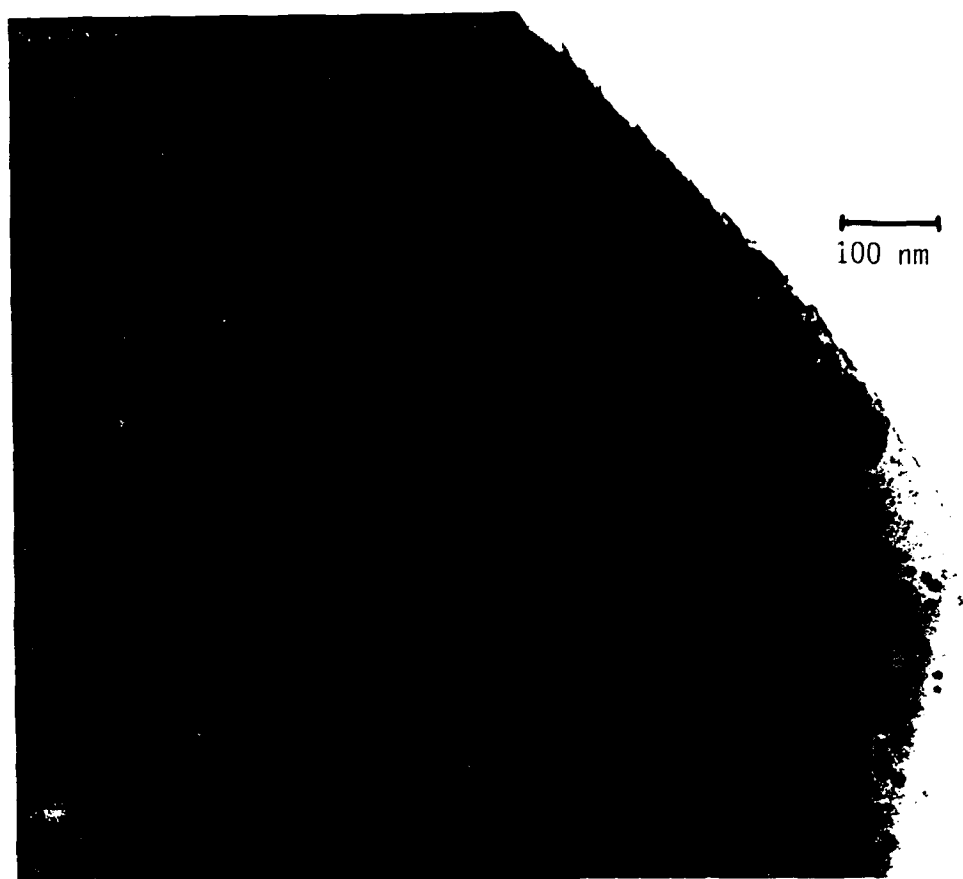


Figure 3. TEM thin section micrographs of densified gel prepared by Method B.